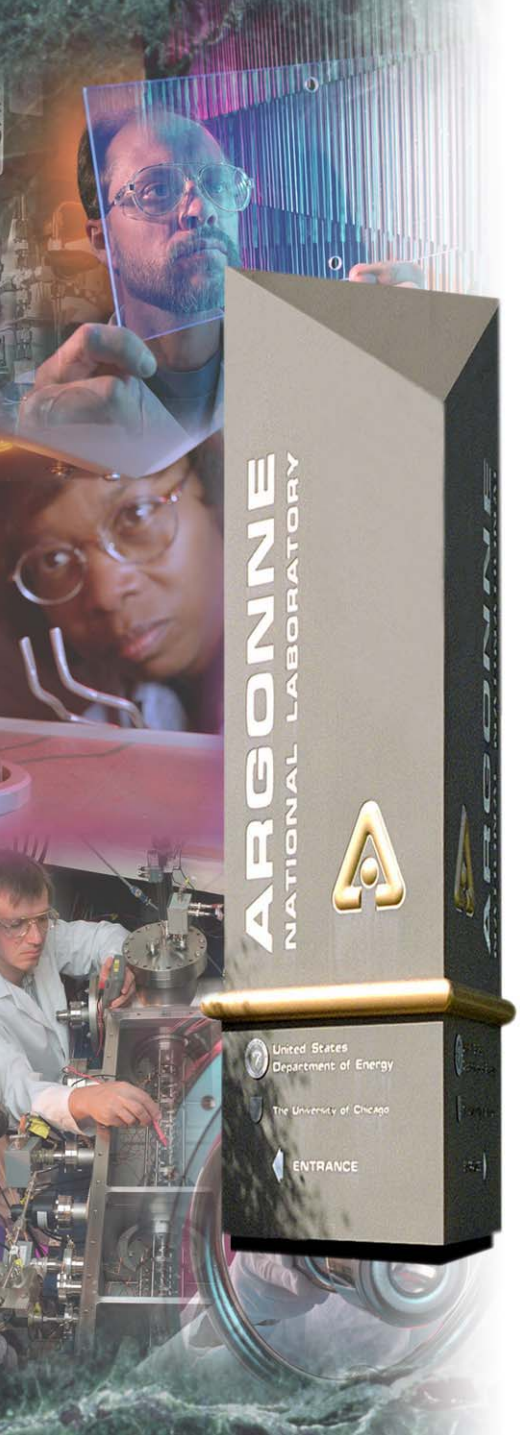


Corrosion of Reactor Pressure Boundary Materials in Boric Acid Solutions

J.-H. Park, O. K. Chopra, K. Natesan, and W. J. Shack
Argonne National Laboratory

January 18, 2005

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Project Objective

- **The overall objective of the program is to conduct research in specific areas focused to determine the conditions that can lead to aggressive and rapid rate of attack of pressure vessel steel in the presence of high concentrations of boric acid in nuclear power plants**

Corrosion-Related Tasks

- **Measurement of Electrochemical Potential (Corrosion potential) of Alloy 600, SS308, and A533.Gr-B in Concentrated Boric Solutions**

- **Corrosion of Reactor Steels in Concentrated Boric Acid Solutions**

Key Subtasks

Establish test facilities for measuring electrochemical potential of A533B, Alloy 600, and SS308, and for potentiodynamic studies

Complete potentiodynamic anodic polarization tests and ECP measurements of A600, 308SS, and A533B, in (a) high-T high-P water with range of boric acid, (b) H-B-O solution at high-T and 1 atm, and (c) low-T saturated boric acid solution

Establish test facilities for corrosion/wastage tests in

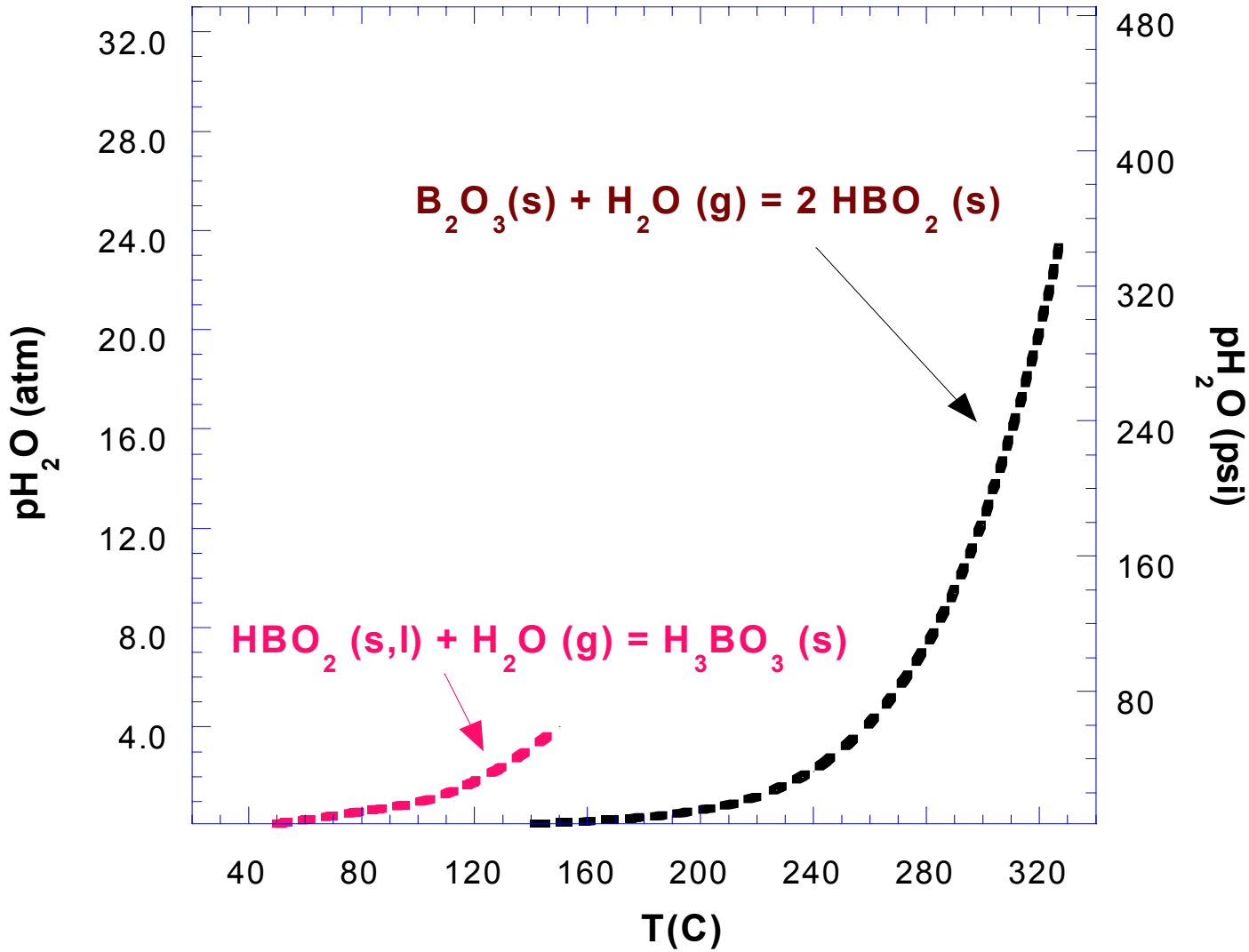
- **high-T, high-P water with a range of boric acid solution concentrations;**
- **high-T H-B-O solutions at 1 atm; and**
- **low-T (97.5°C) saturated boric acid solution, both in non-aerated and aerated conditions**

Perform wastage tests of A533.Gr-B vessel steel and 308SS clad in the three environments

Phases present in the B-O-H system

Phases	T (°C)	Reaction with H_2O
H_3BO_3	169 (tr)	$B(OH)_3 + H_2O = [B(OH)_4]^- + H^+$
HBO_2	236(mp)	$B(OH)_3 - H_2O = HBO_2$
B_2O_3	450(mp)	$HBO_2 - 1/2\ H_2O = 1/2\ B_2O_3$

Equilibrium pH_2O vs. T in the H-B-O system



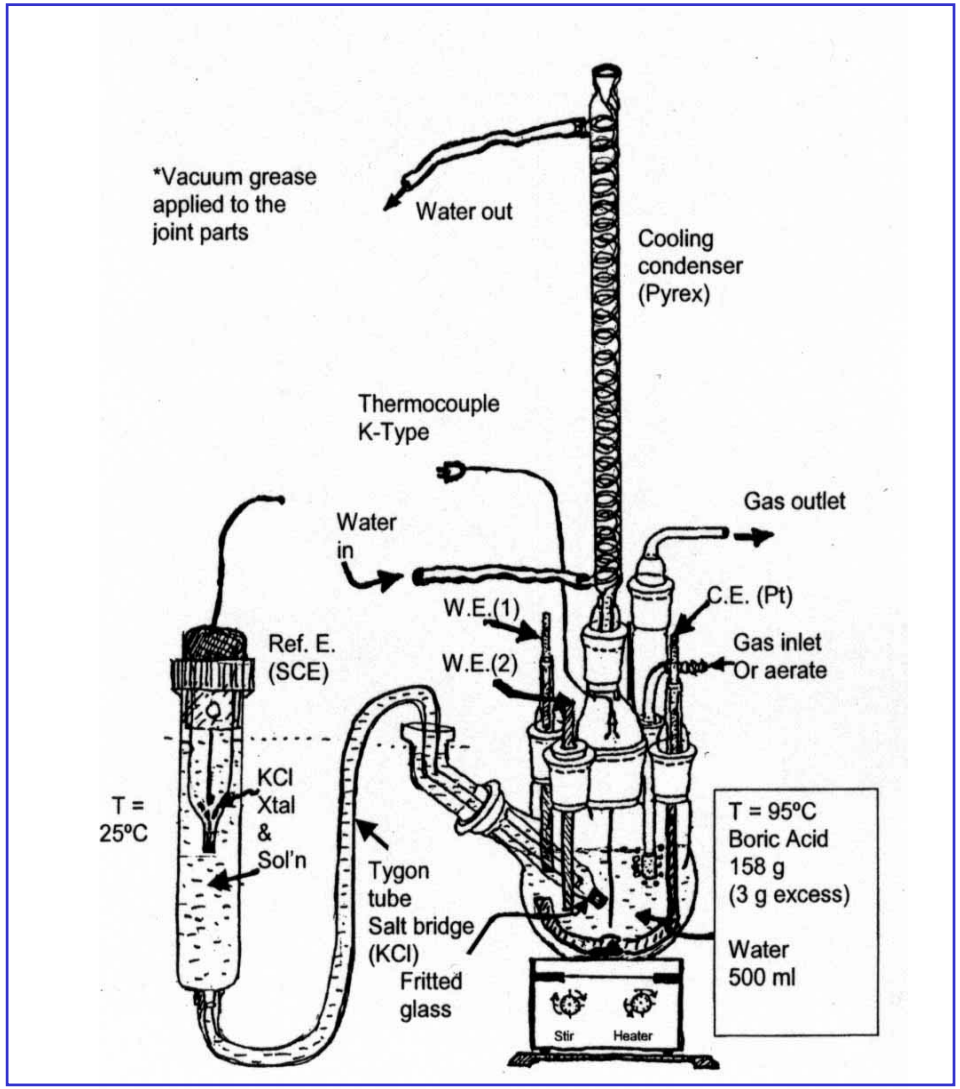
Tests in

Aqueous Boric Acid Solutions

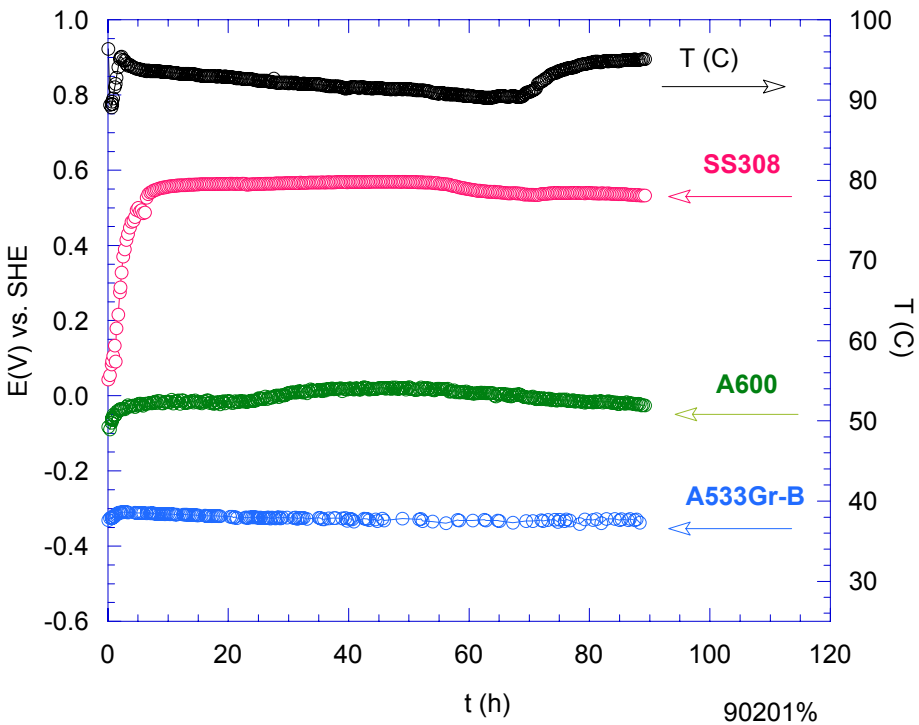
Experimental Electrochemical Cell for ECP Measurements & Potentiodynamic test

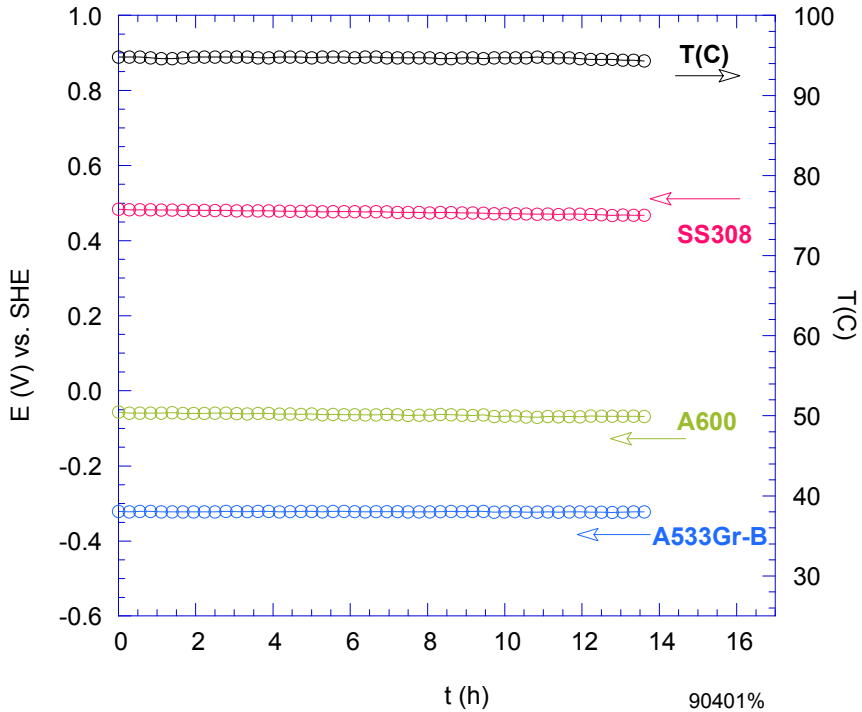
Tests were performed in BA solution at ≈100°C

- **Measured ECPs and performed PD-test**
  -Specimen (bar shape)
  -Sol'n stirred (magnetic stirrer)
- **PH measurement on the Sat'd BA solution at rt to 100°C**
- ***PH measured in (de/ae)rated BA solutions**



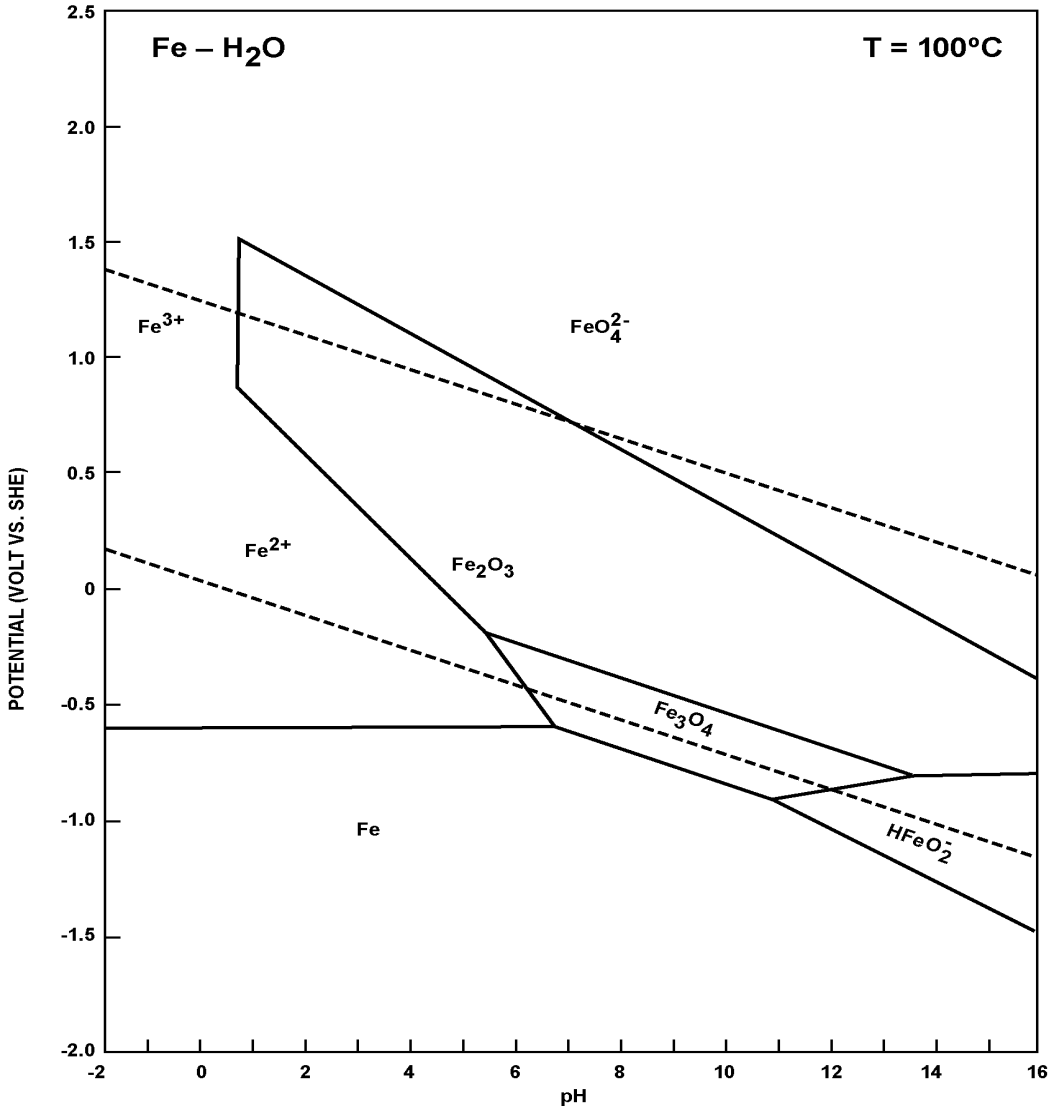
E(V) vs. time in the sat'd BA sol'n @97.5°C





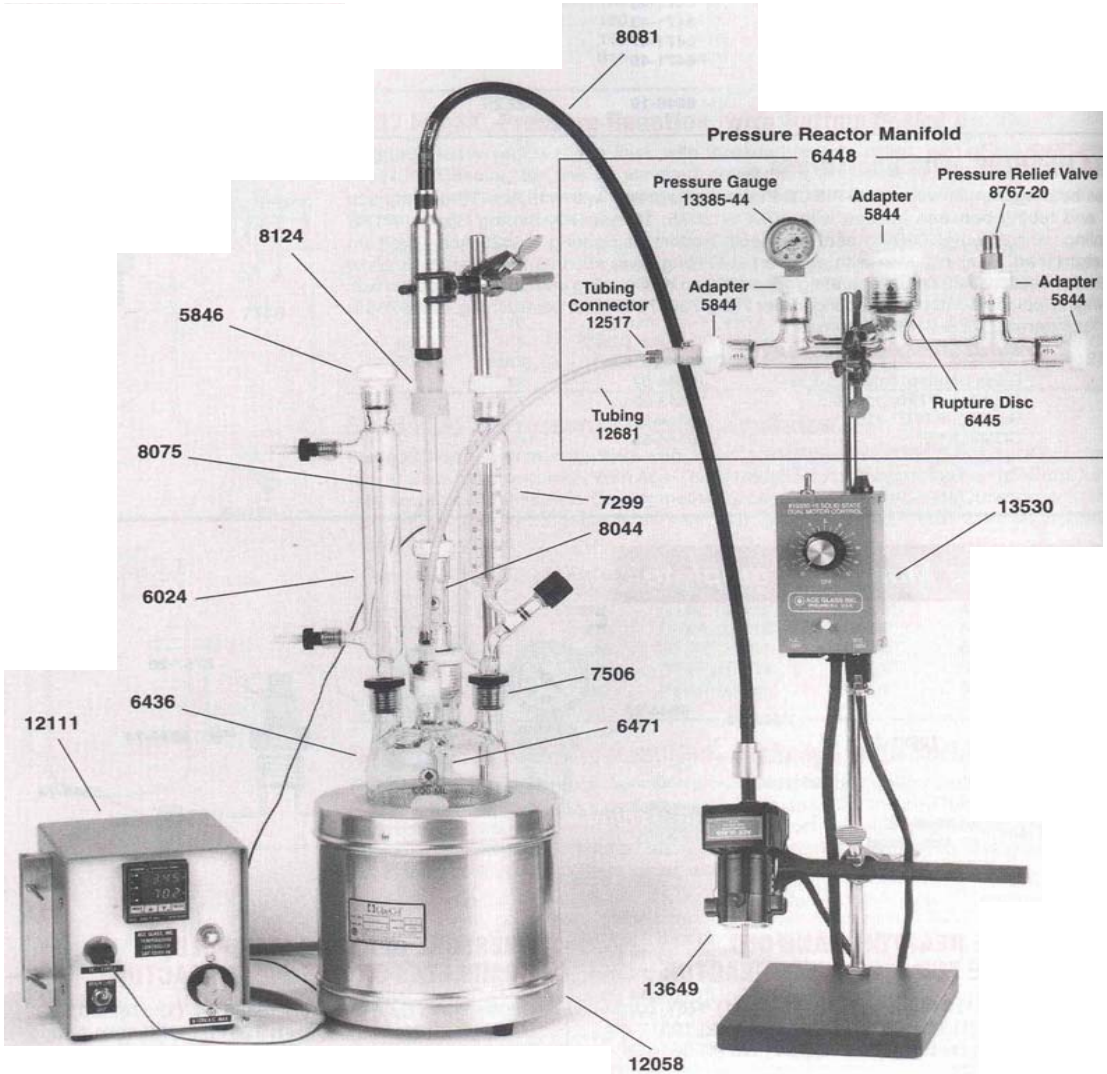
After the initial 90 h

E_H vs. pH for Fe-O-H @ 100°C *(Ref. EPRI)*



Pioneering Science and Technology

Measurement of Wastage for A533Gr B @ 97.5°C

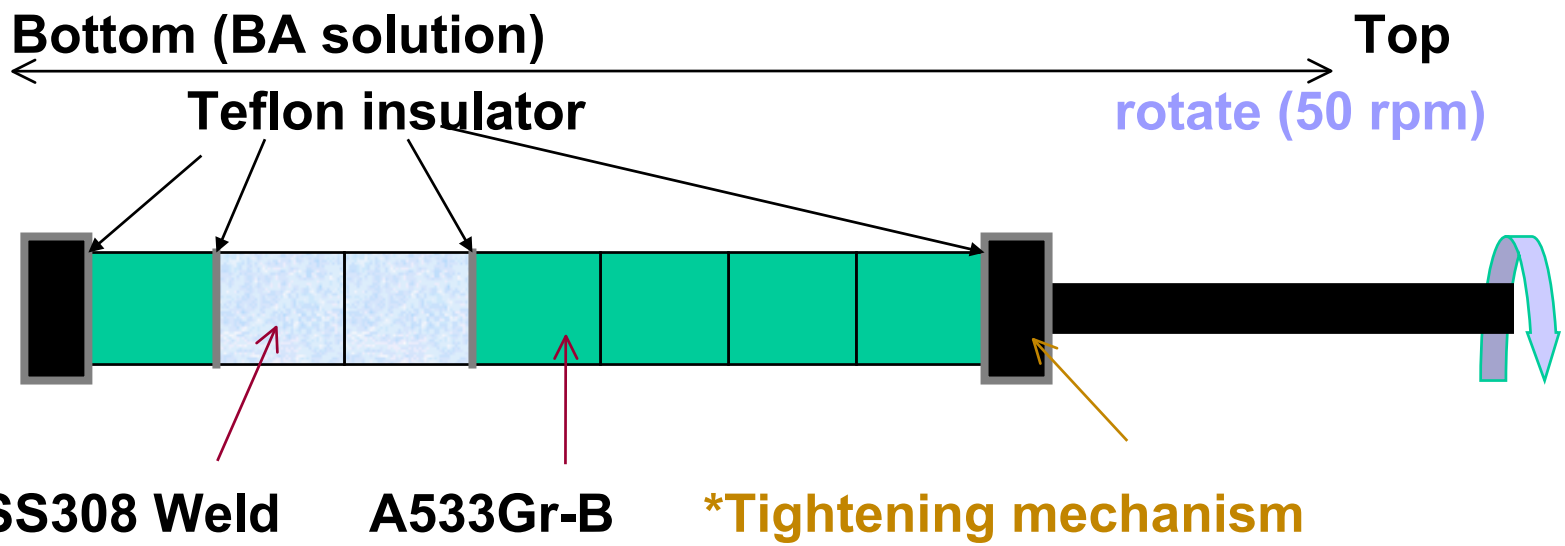


Pioneering Science and Technology

Wastage test sample assembly in solution

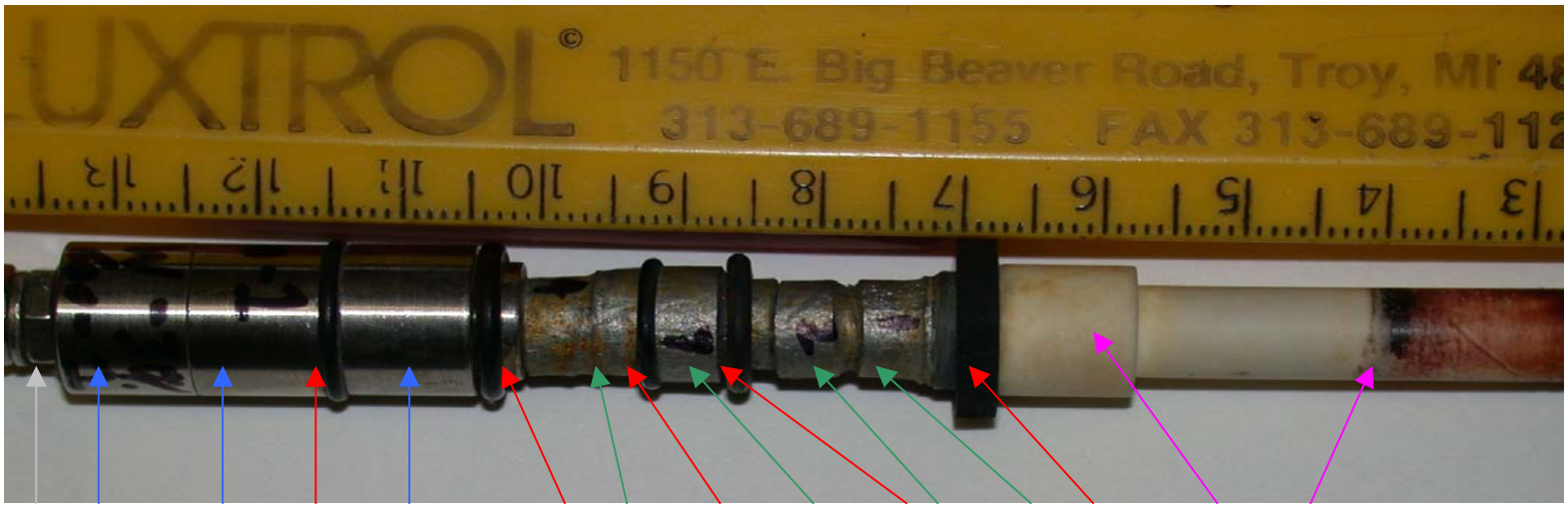
Sample: 6.5 gram, OD (0.50”), ID (0.275”), length (0.5”)

plug shape



***Stack inside leak-tight filled with rubber tube between shaft**

Sample stack view for A533Gr-B, A600, SS308 after exposure for 311 or 411 h in sat'd BA solution at 97.5ºC



A B C D E F G H I J K L M N O

A: Screw tightening mechanism with flat O-ring a the bottom

B: A600 (30%CW), C: A600-1, E: SS308 clad weld

D,F,H,J, & M: O-rings,

G, I, K, & L: A533Gr-B #1,2,4, &7.

N & O: Alumina (N, in the solution & O, interface solution/vapor)

Corrosion Rate Conversion: $Fe \rightarrow Fe^{2+} + 2e'$

$$CR\ (mm/yr) = [0.306\ nd/M] * J_{Corr}$$

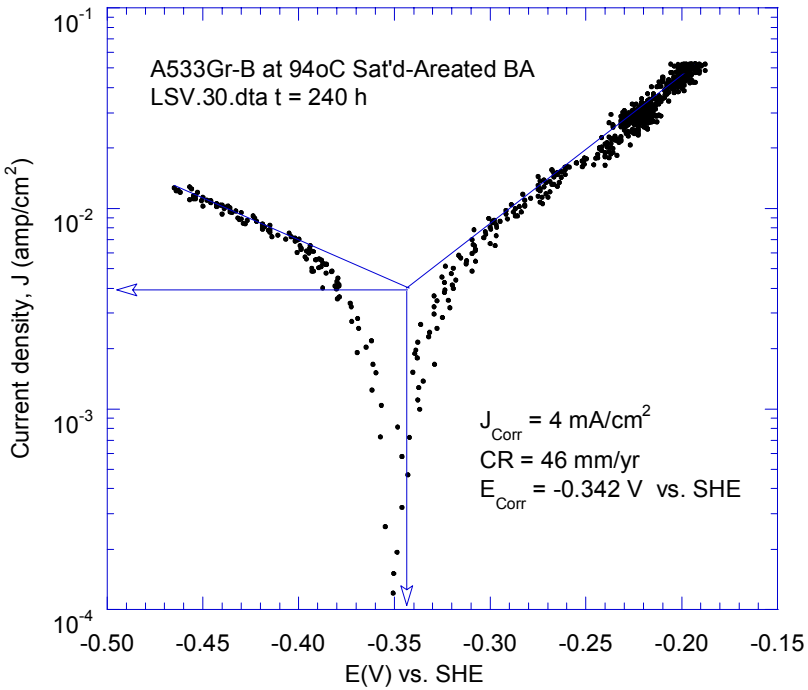
- CR (mm y^{-1}) =Corrosion rate
- J_{corr} (mA cm^{-2}) =Corrosion current
- n = # of electrons freed by the corrosion reaction
- M = atomic mass, d = density

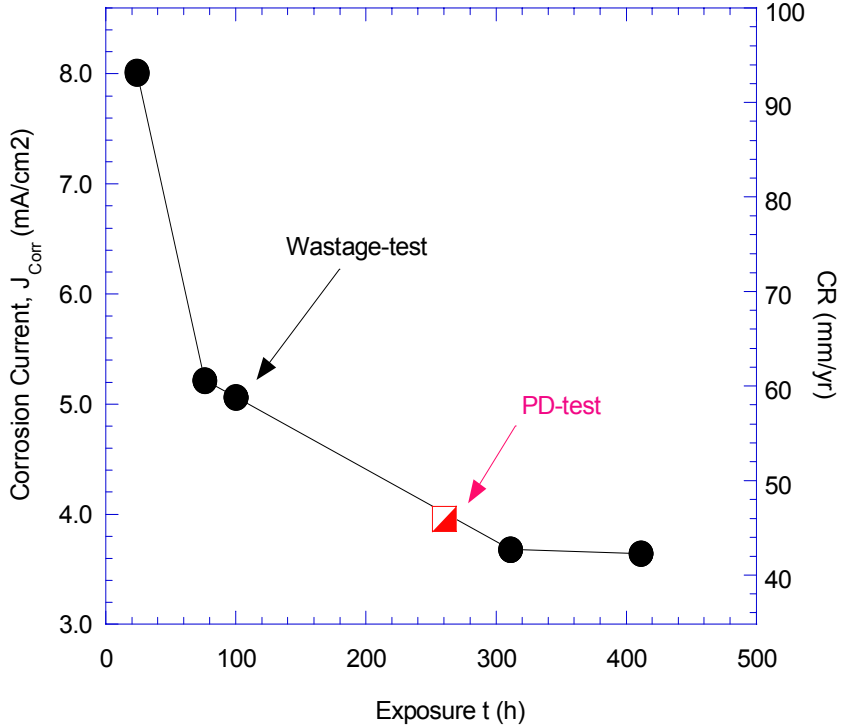
For steel:

- n =2, M = 55.85 g and d = 7.88 g cm^{-3}
- $CR\ (mm/yr) = 11.6 * J_{Corr}$

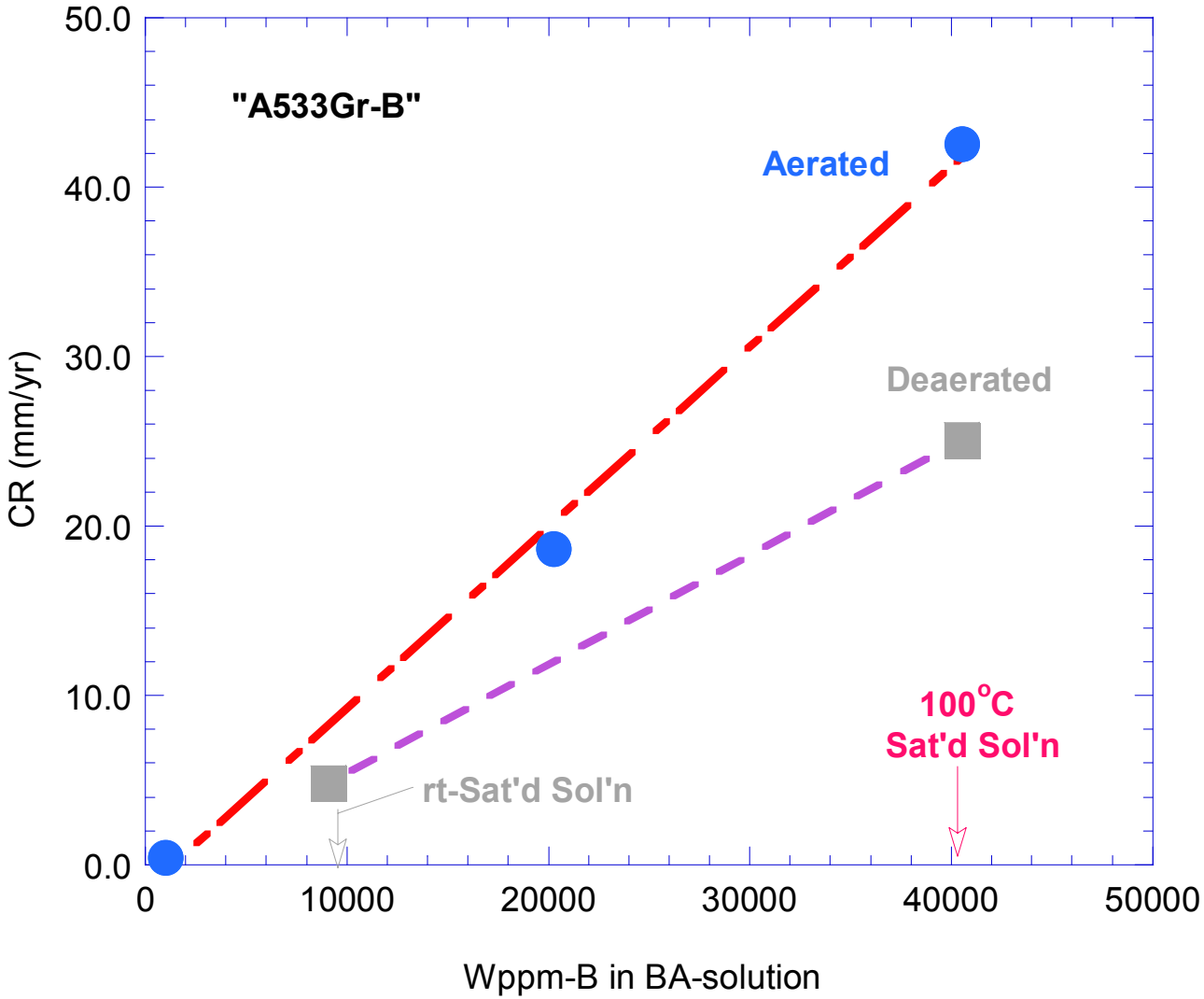
PD-test of A533Gr B in Sat'd BA soln at 97.5˚C

- 42,000-ppm B (Sat'd BA)

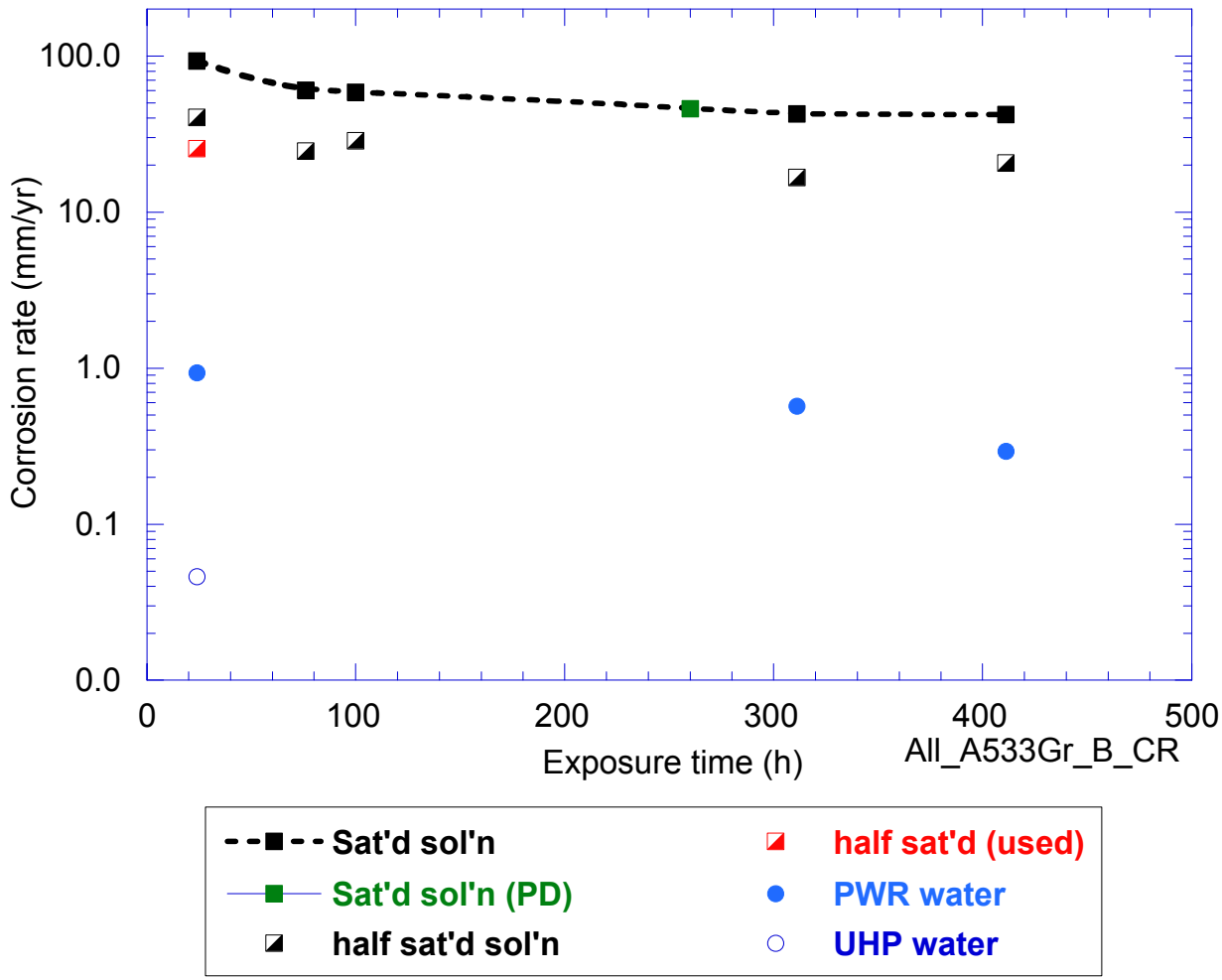




Corrosion rate vs. Wppm-B for A533-Gr. B in aerated and deaerated BA solutions near 100°C



Wastage rates for A533Gr-B Steel in BA solutions at 97.5°C



Corrosion Tests in H-B-O Solutions At T > 100°C

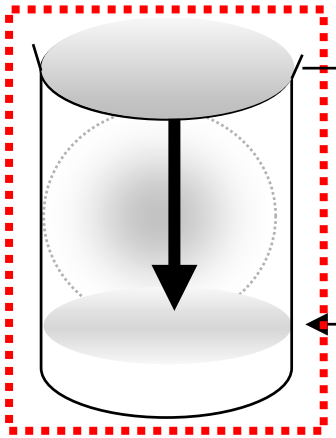
Corrosion Tests in H-B-O

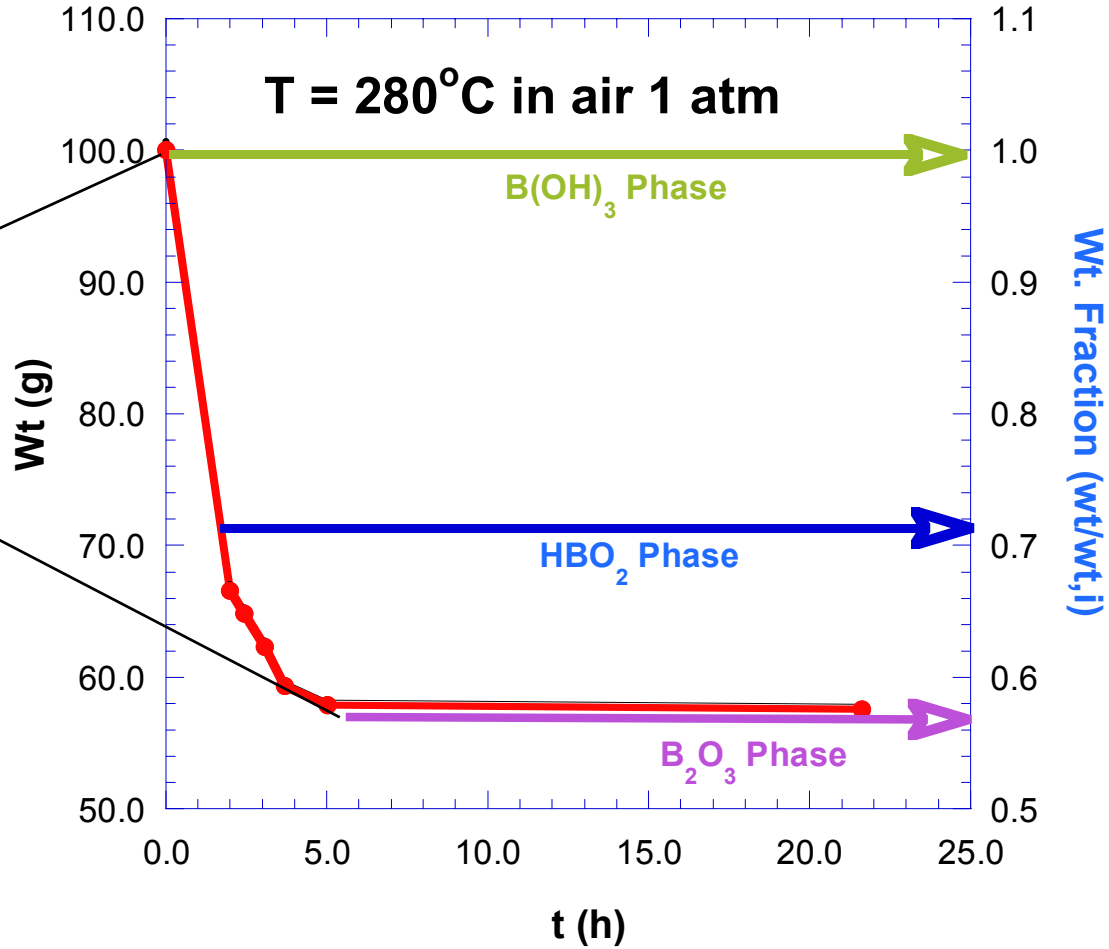
150 ≤ T ≤ 300ºC in aerated condition

1. Dry boric acid: 170 ≤ T°C ≤ 300 : Molten Salt
   - I) T = 300 ± 9°C
   - ii) T = 260 ± 7°C
   - iii) T = 154 ± 4°C
2. Wet boric acid: water addition: Sat'd BA @T
   - iv) T = 150°C
   - v) T = 170°C

Boric acid heated in ambient at 280°C

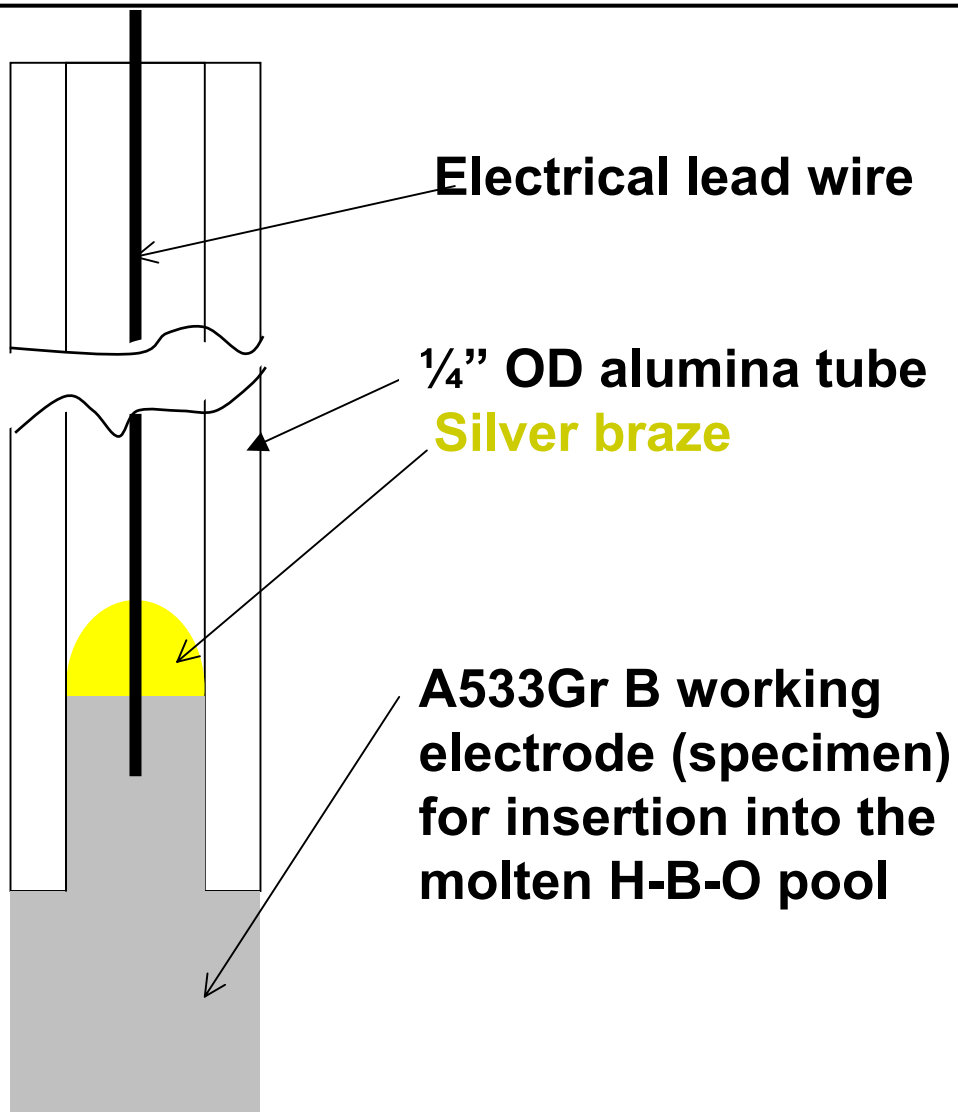
Boric acid turned to snow-ball shape and then glass like transparent boric oxide collected in the bottom of the beaker by loosing water.



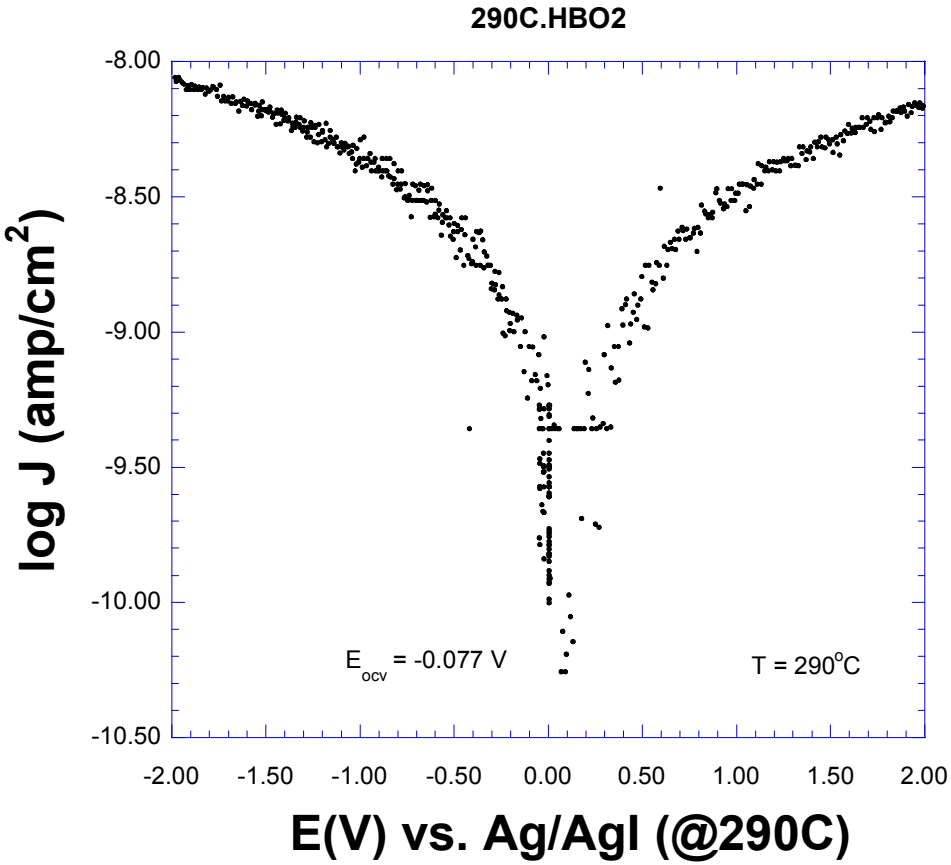


Note:100-g Boric acid heated in air (pH_2O = 3%) at 280°C

Test in H-B-O Solutions
Specimen (Working Electrode)



PD-test Ambient $HBO_2 + B_2O_3$ (Dry)



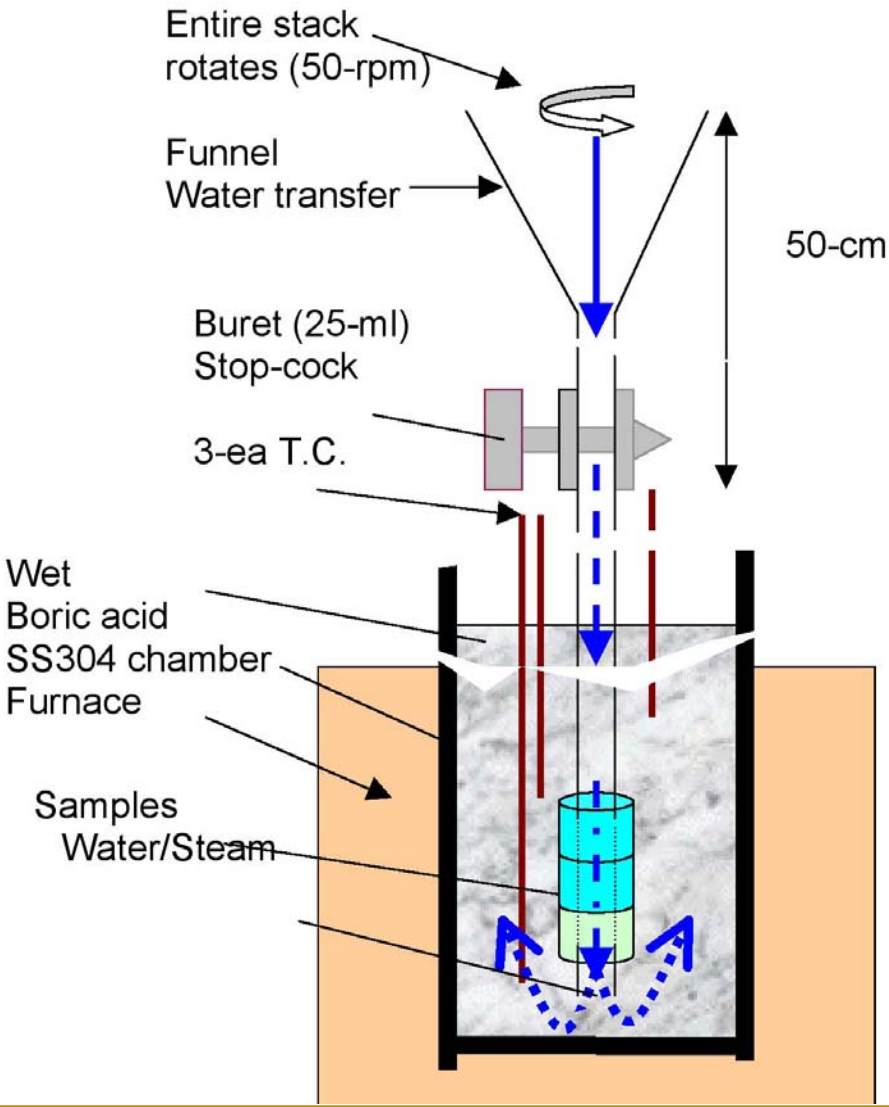
Overnight air equilibrium @ 290ºC.
Measured current density indicates that A533Gr B is highly protective.

Corrosion in Ambient H-B-O ($150 \leq T^{o}C \leq 300$):
Dry Condition

PD-Test & Corrosion Tests

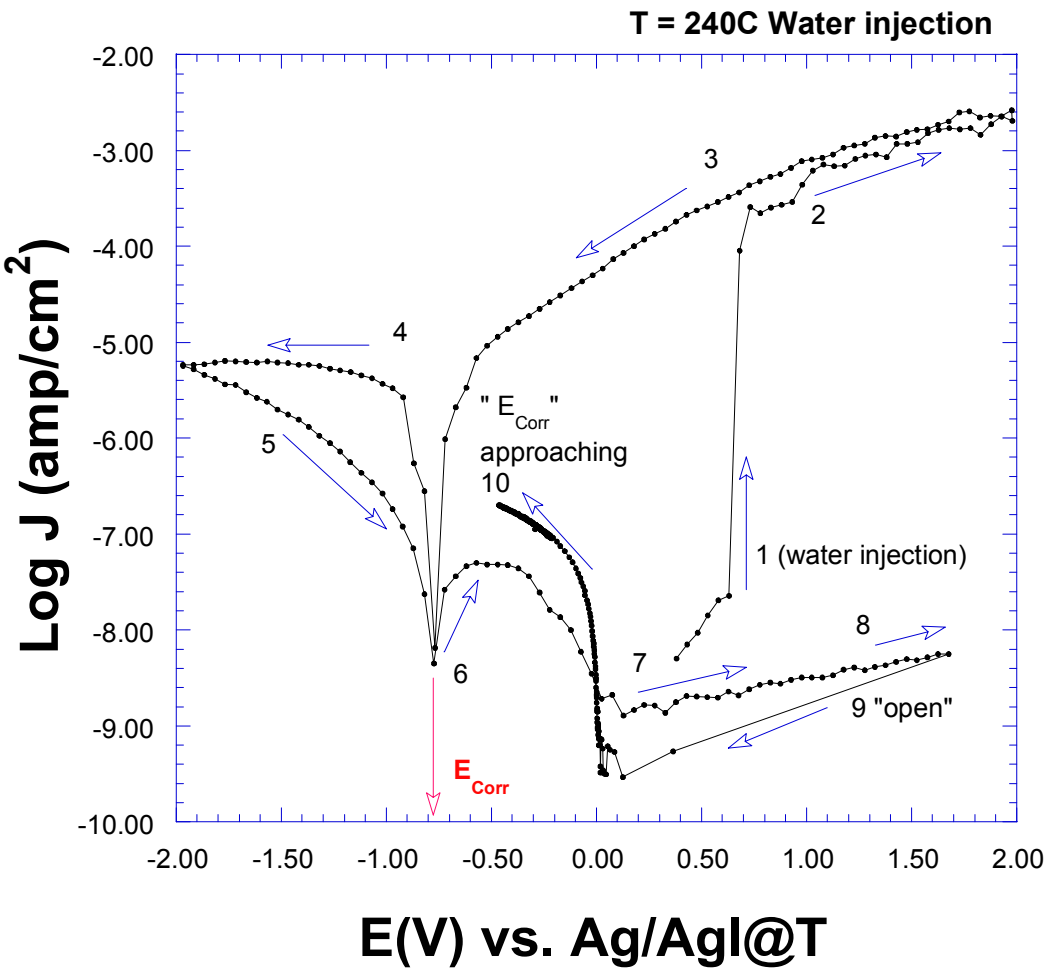
"No Corrosion"
On
A533Gr.B, A600, SS308
in the Absence of Water

Wastage test apparatus for the Water Adding H-B-O system

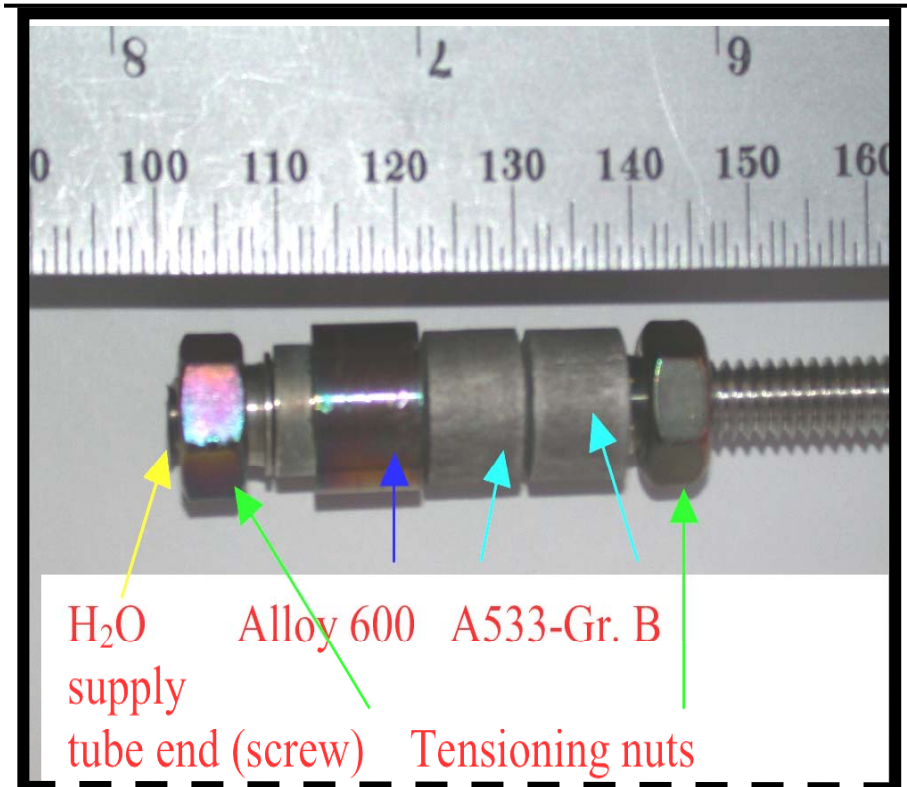


PD-test: Water Adding $HBO_2 + B_2O_3$

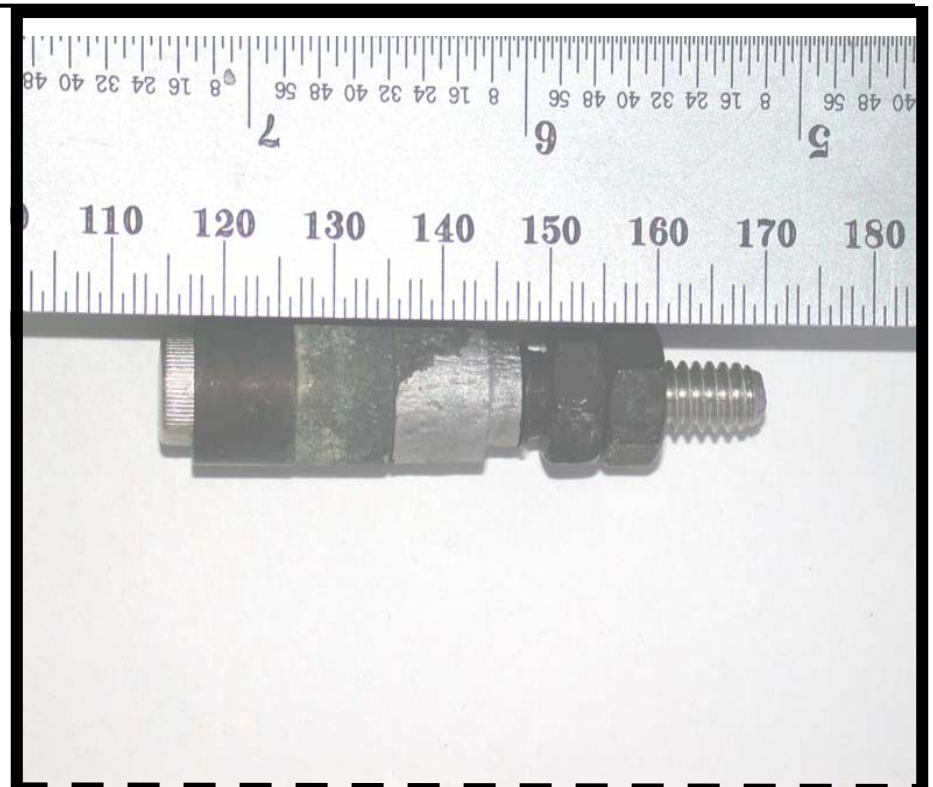
- ***Adding water into the test cell***



150 and 170 °C with water additions for test times between 40 and 45 h.

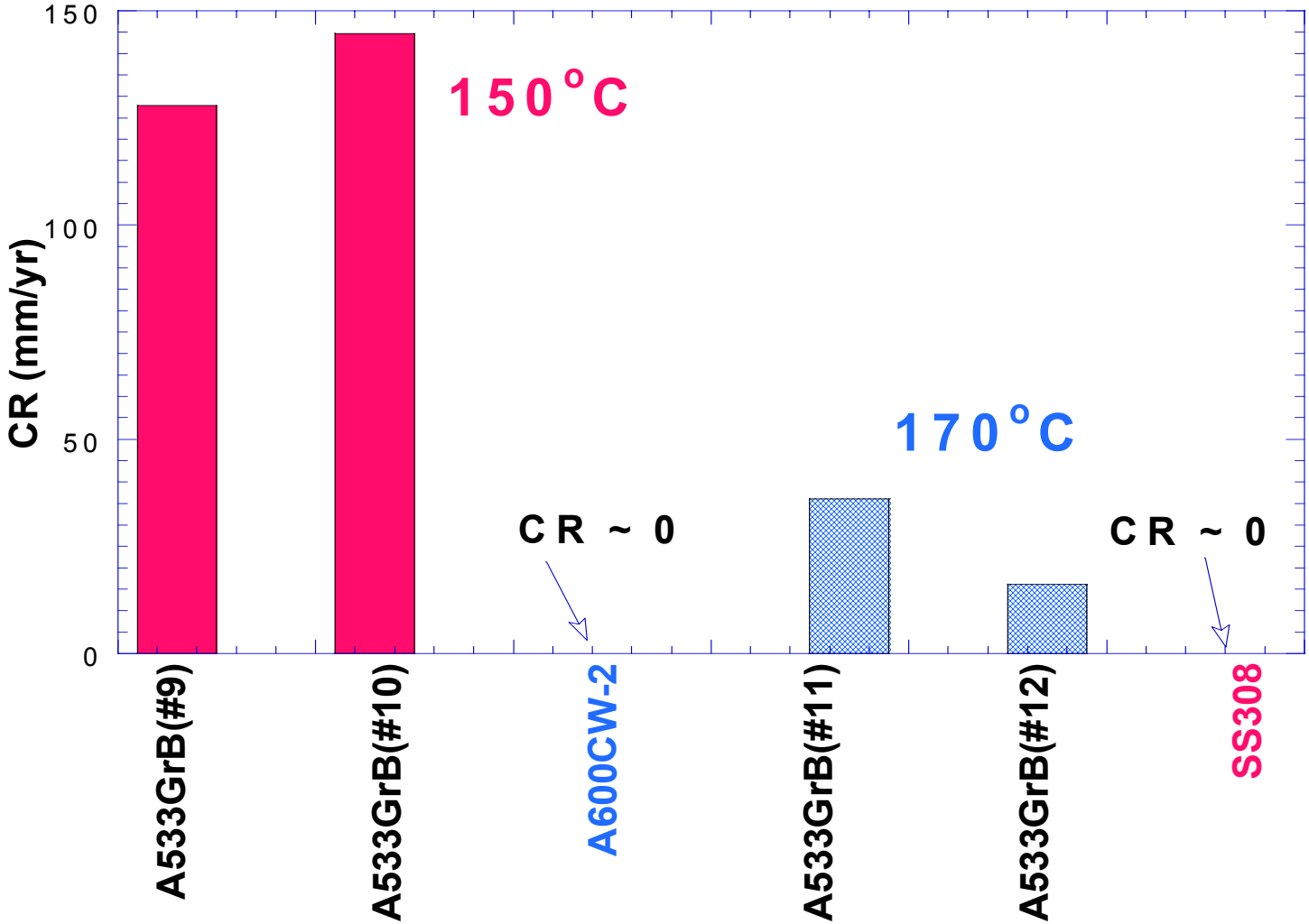


T = 150 °C
water additions for test times between 45 h.

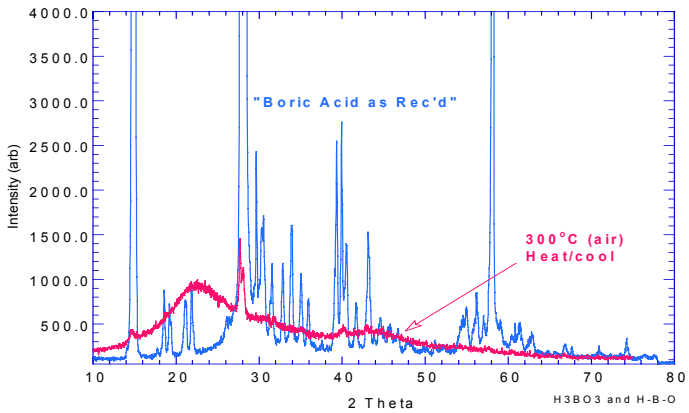


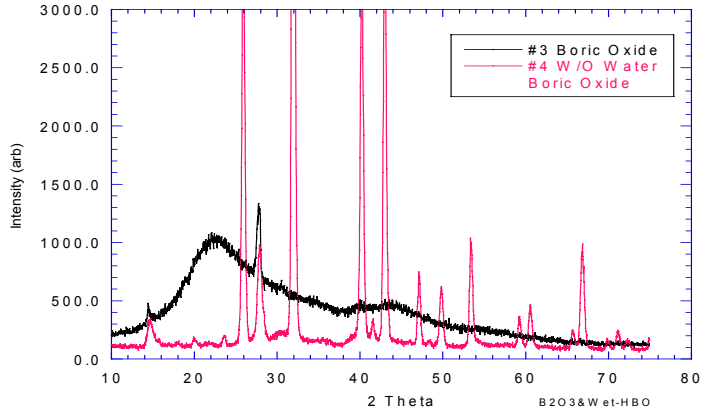
T = 170 °C
water additions for test times between 40 h.

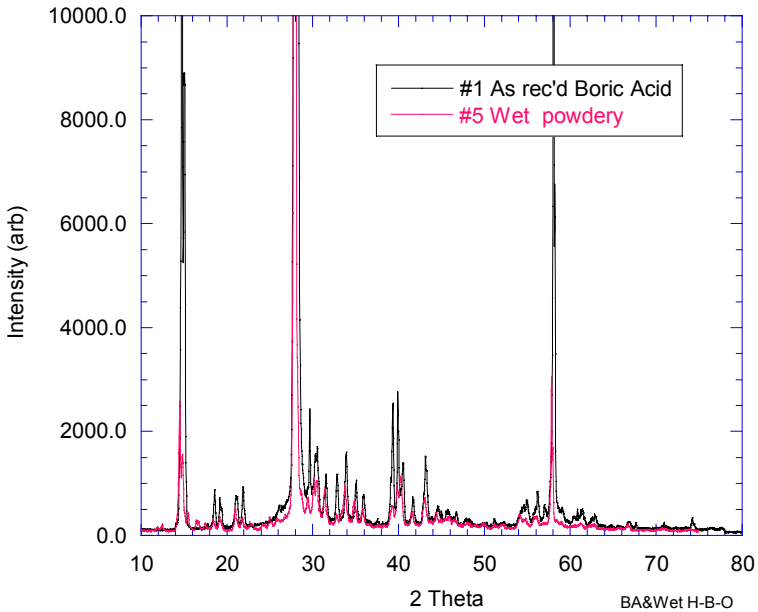
150 and 170 °C with water additions for test times between 40 and 45 h.

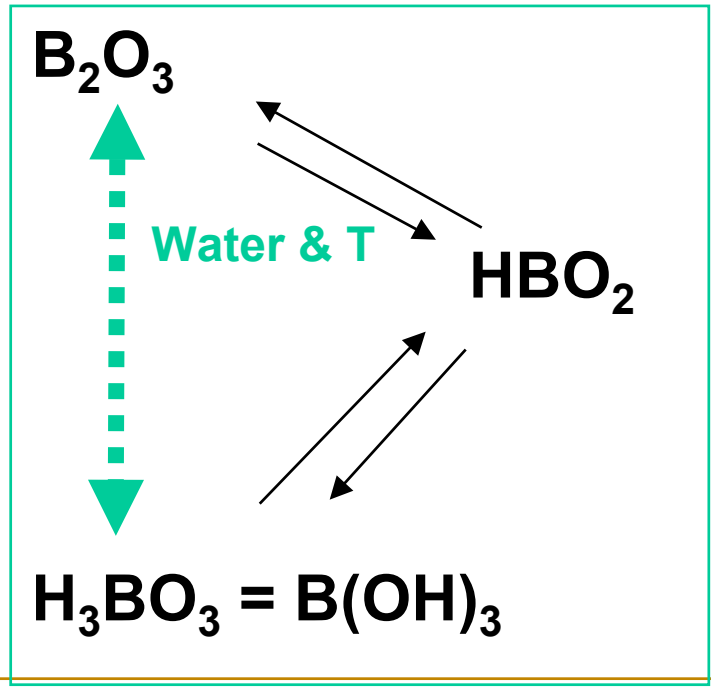


XRD: Boric Acid Cycles with H_2O and T



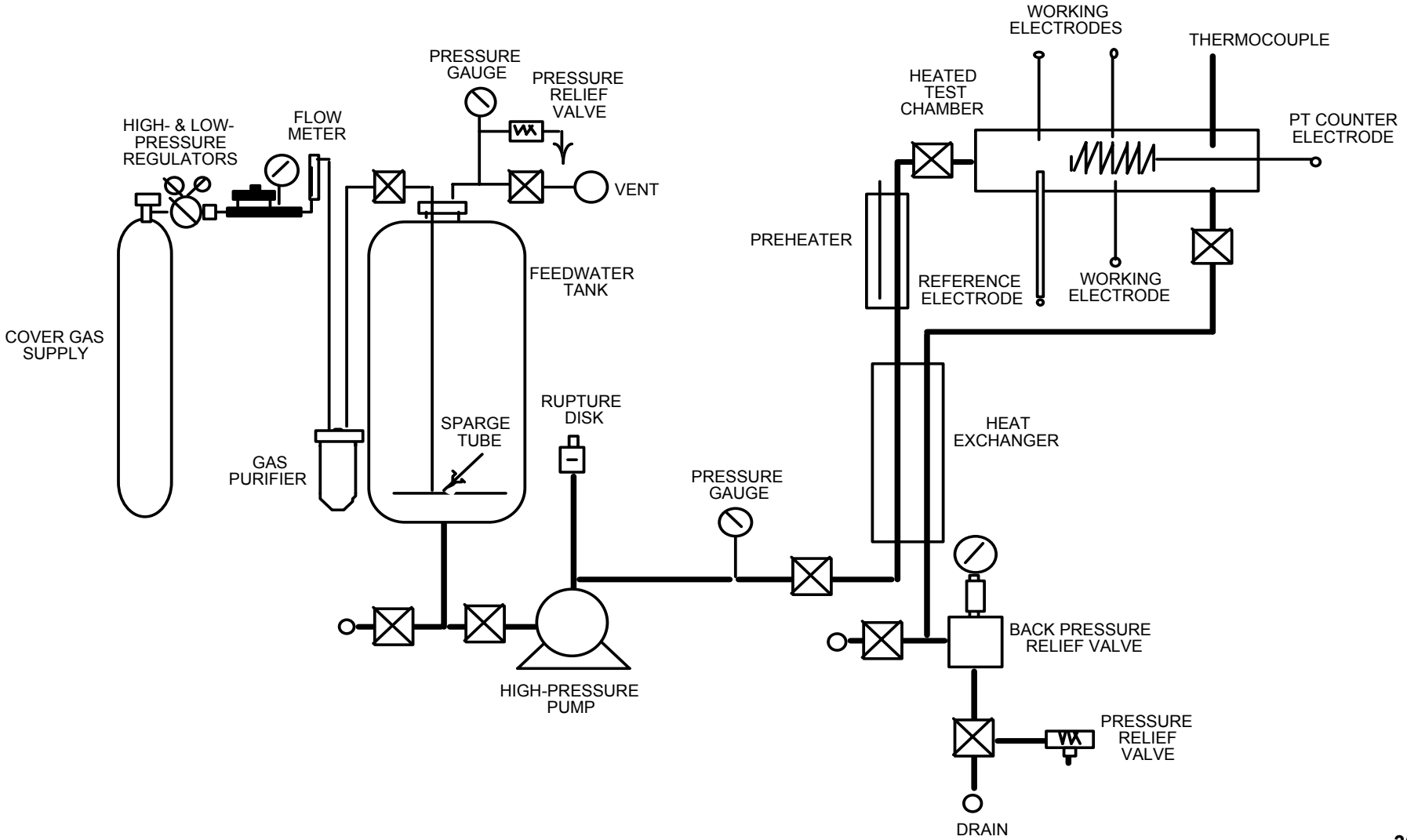




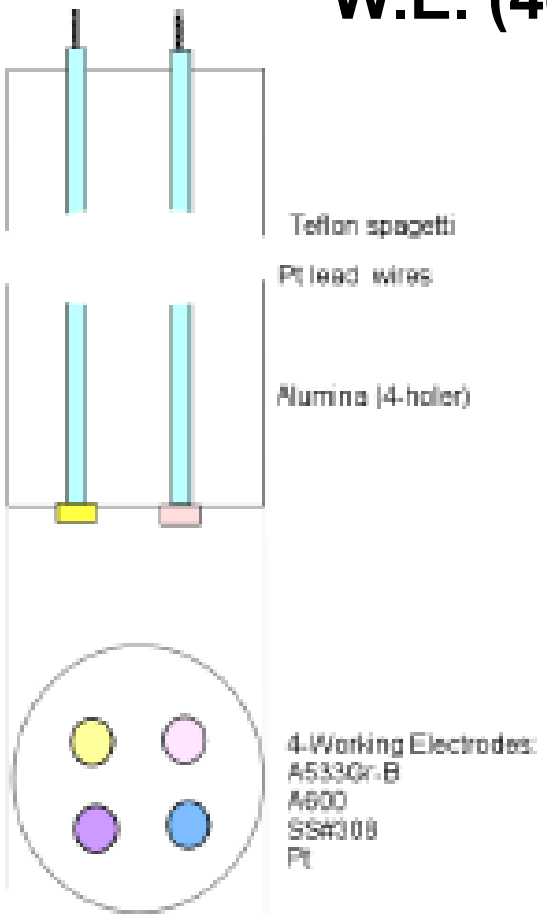


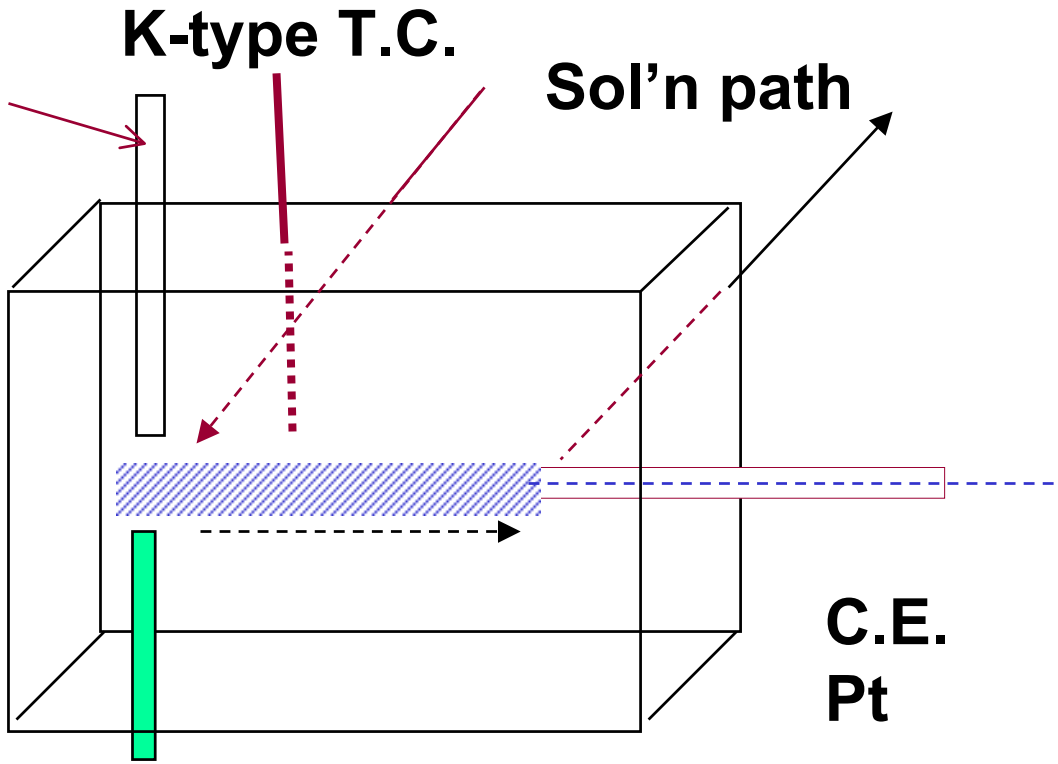
Tests High-T & High-P Aqueous RT-Saturated Boric Acid Solution

Corrosion facility for tests in High–T & P of BA solutions at T up to 316°C



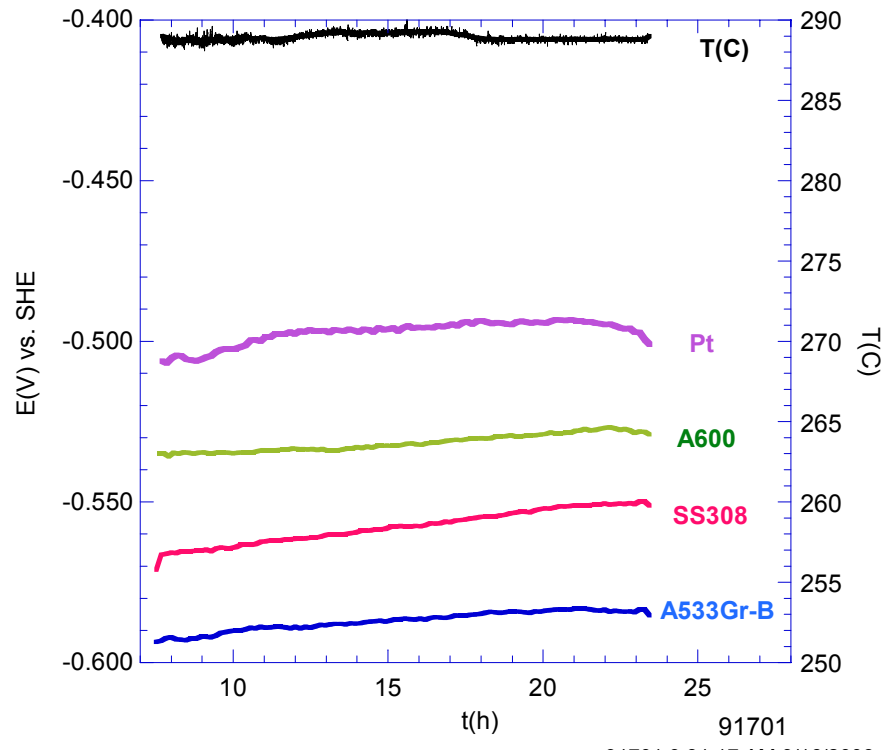
ECP & Corrosion Tests at High T & P

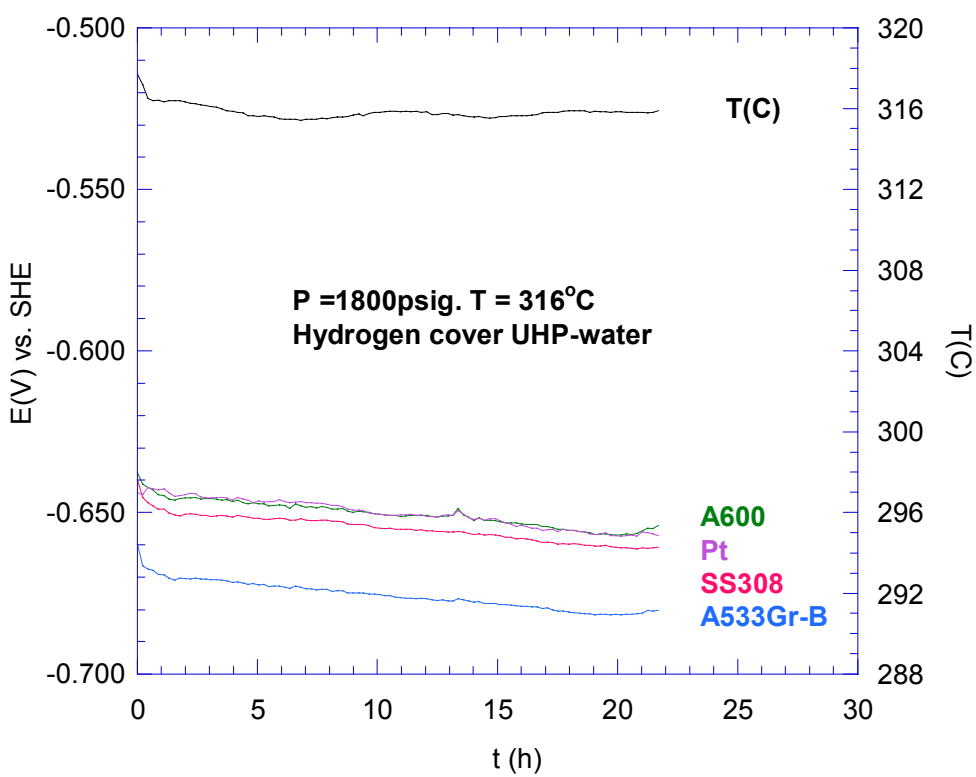




Ref. E
Ag/AgCl-0.1 Mol KCl

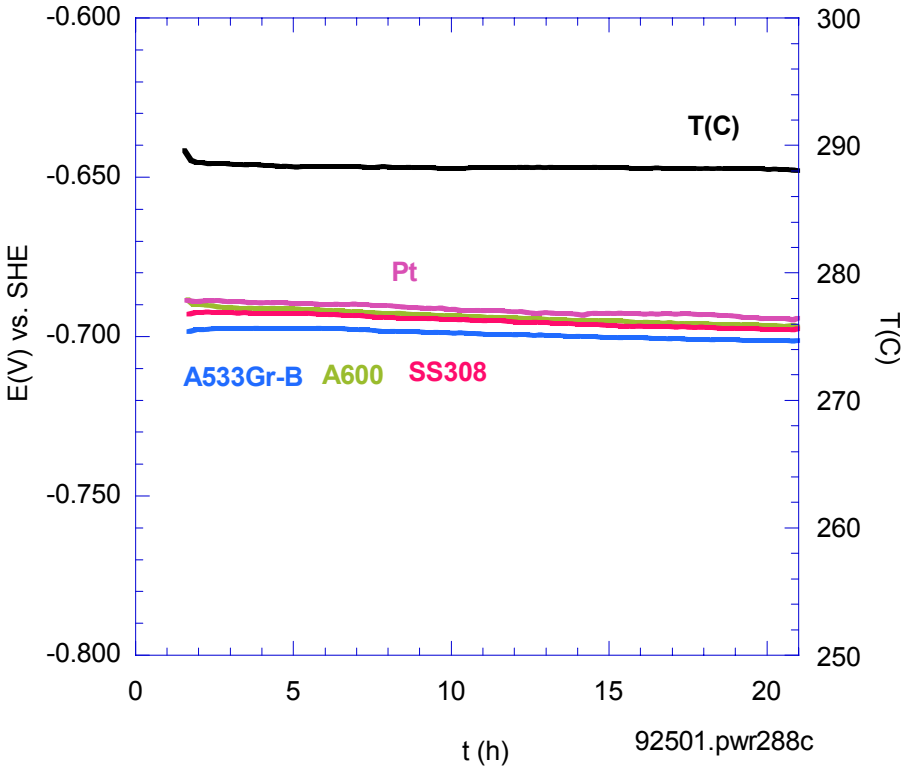
ECP for A533Gr-B, A600, SS308, and Pt in the hydrogen covered UHP-water at 288 &316ºC

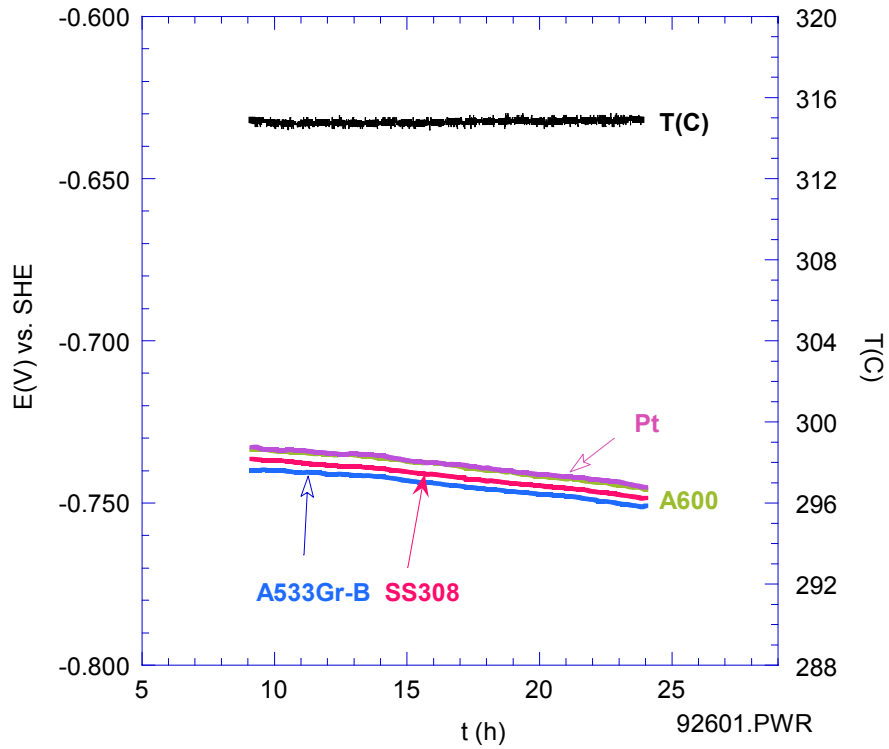




Pioneering Science and Technology

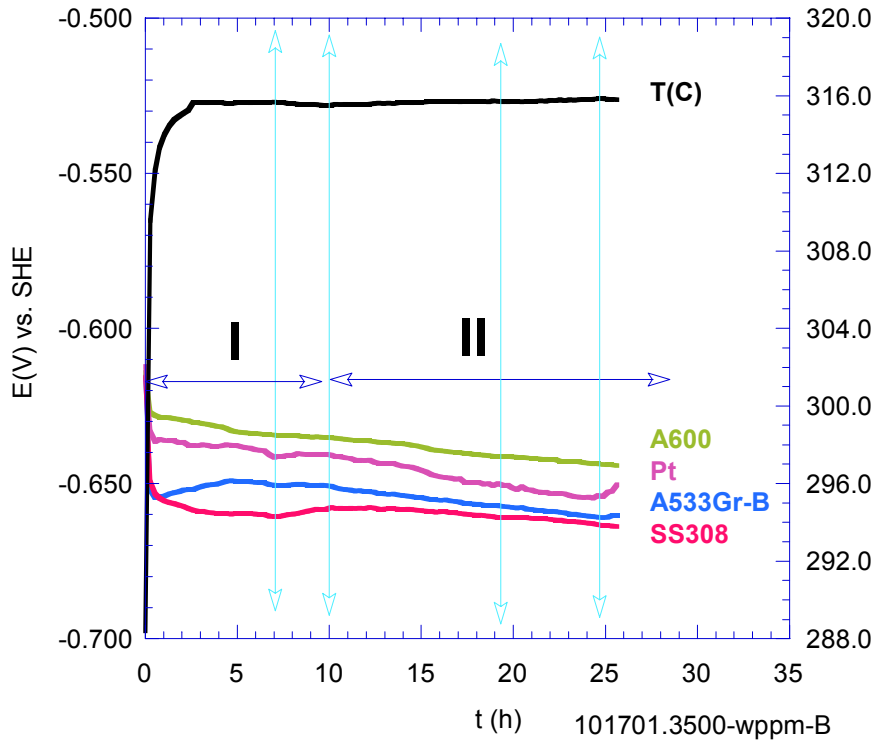
ECP for A533Gr-B, A600, SS308, & Pt in the hydrogen covered PWR-water at 288 & 316ºC

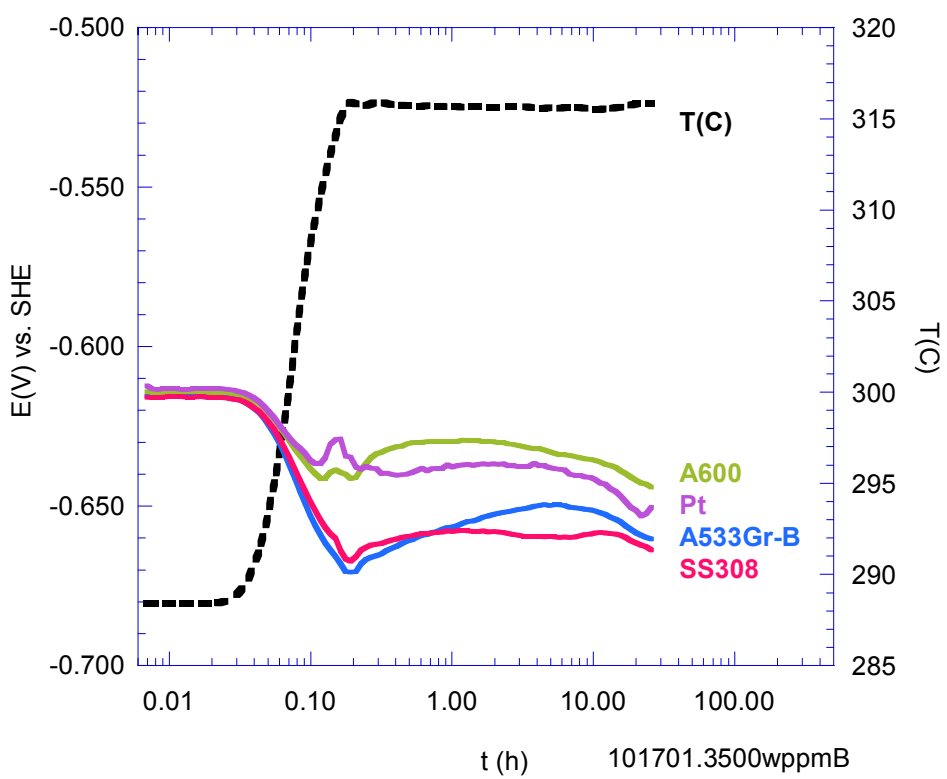




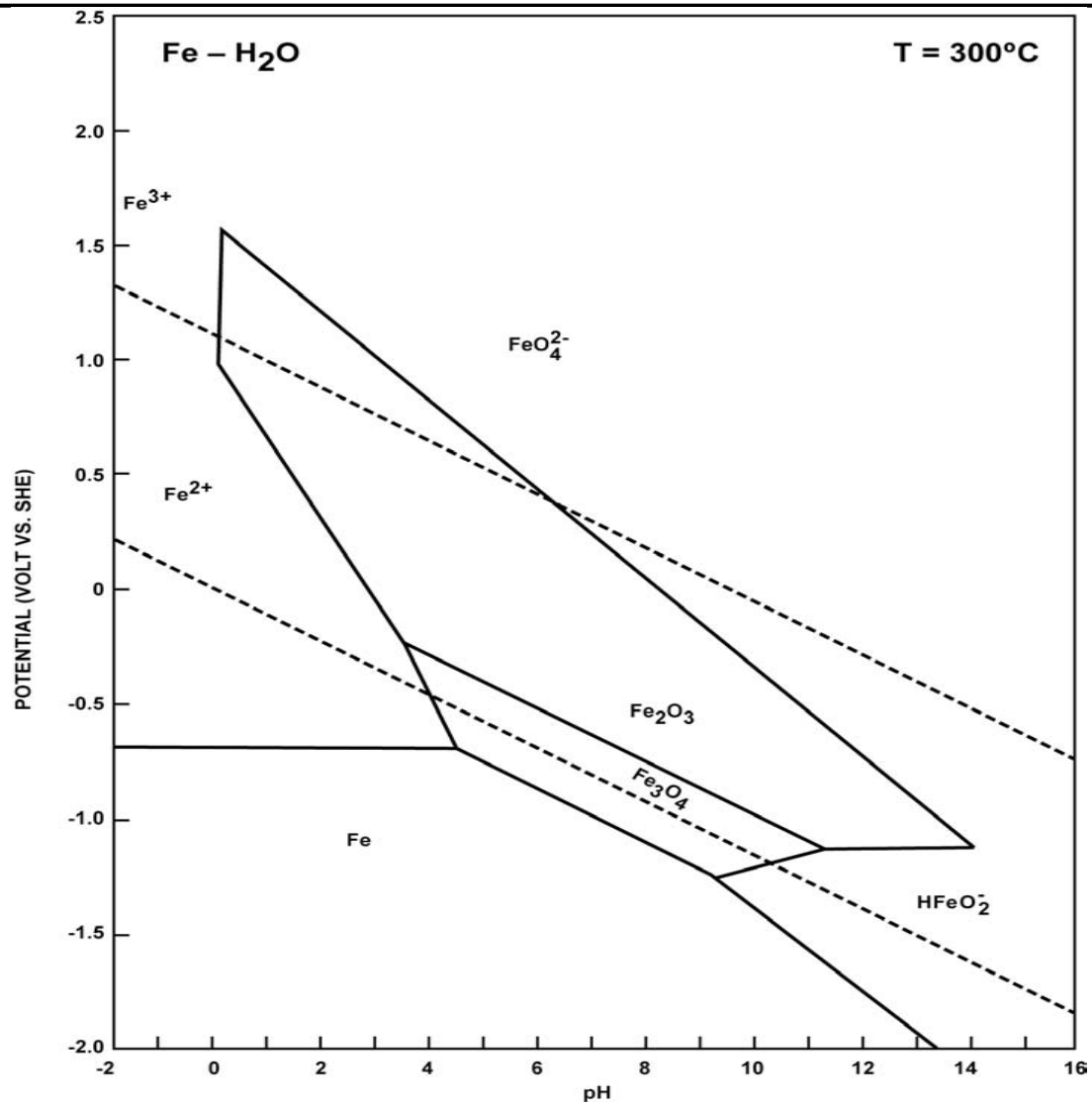
Pioneering Science and Technology

ECP for A533Gr-B, A600, SS308, and Pt :hydrogen covered 3500-wppm-B, 2-wppm-Li at 288/316 ºC

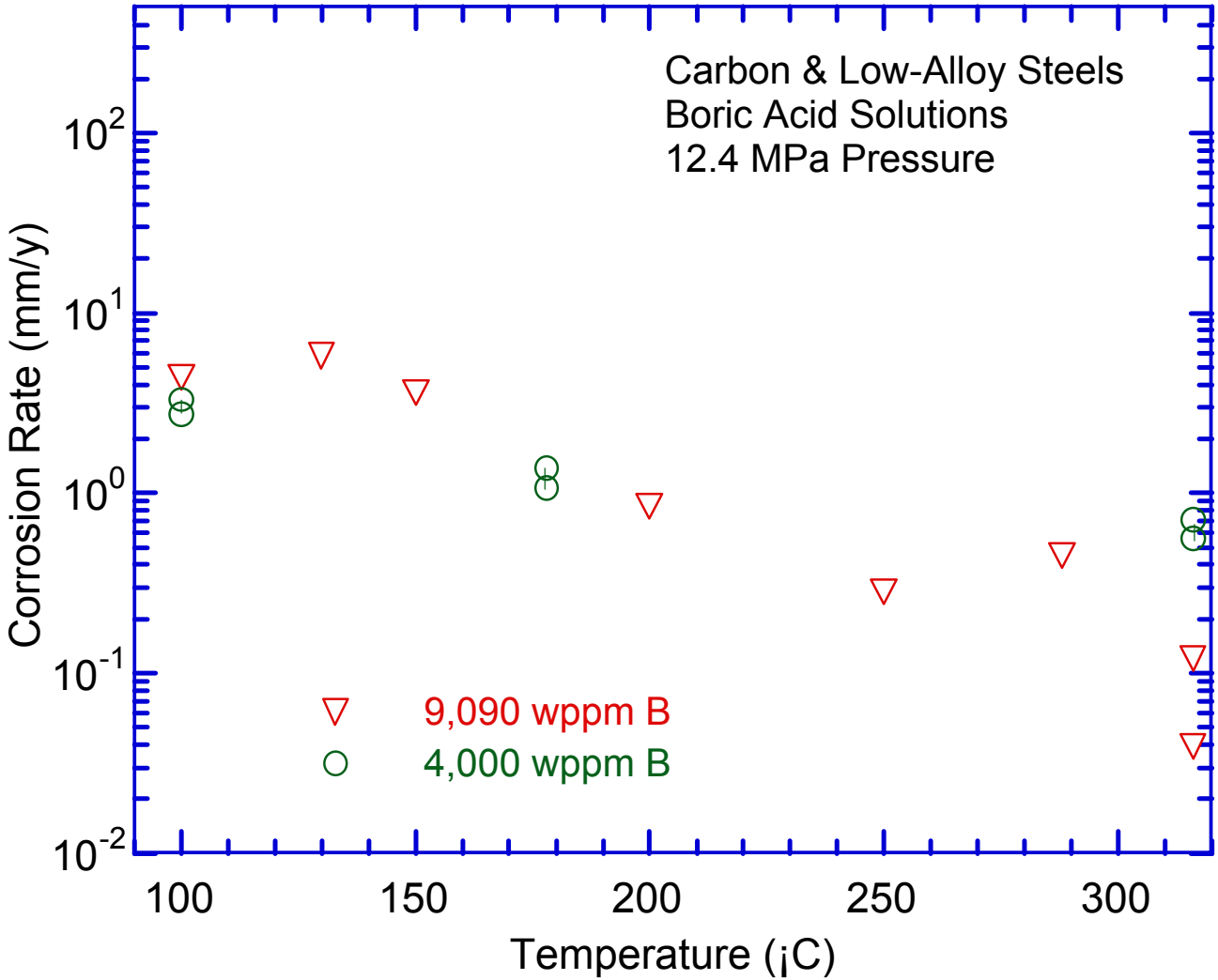




E_H vs. pH for Fe-O-H @ 300°C (Ref. EPRI)

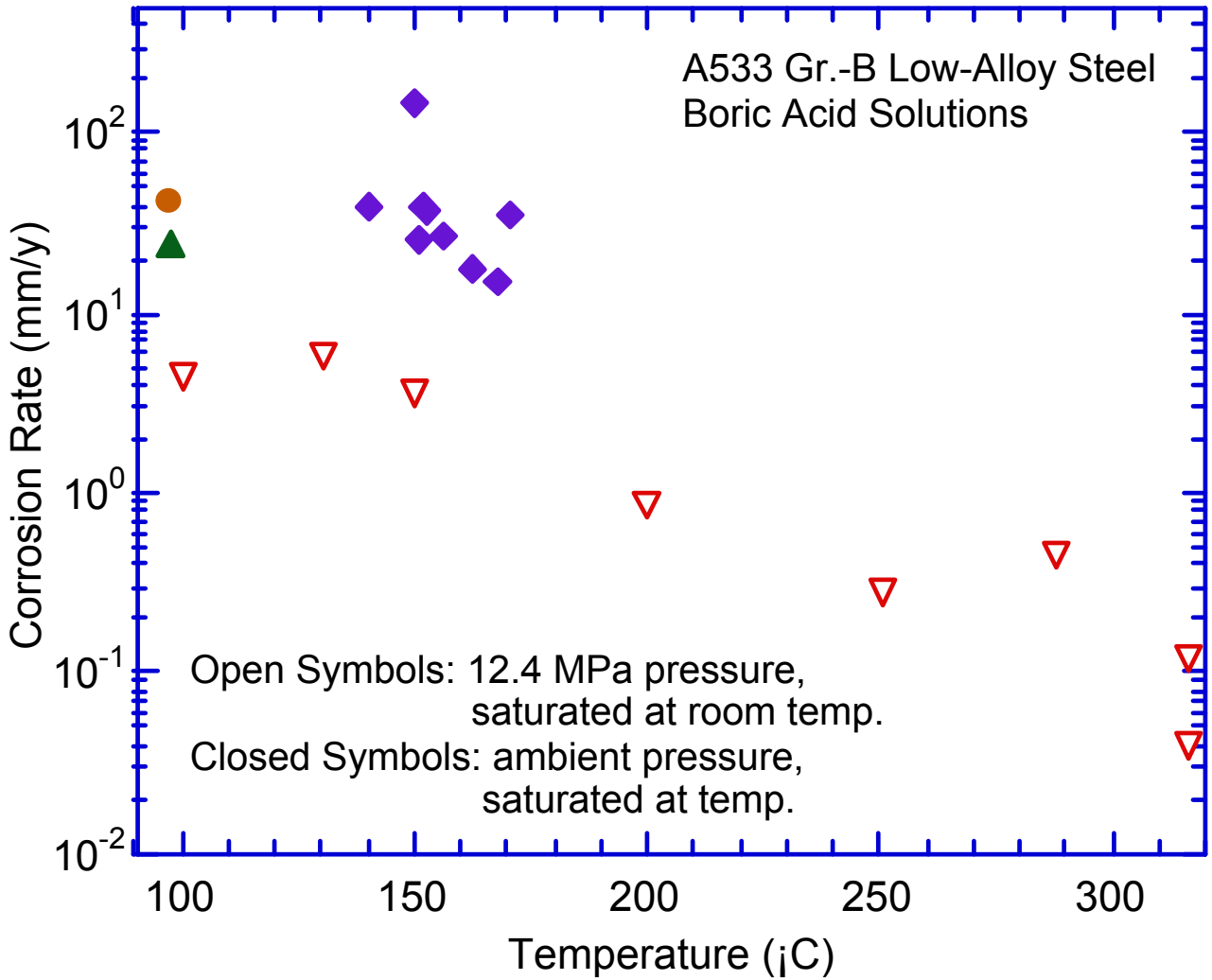


Measured Corrosion Rates for Carbon and Low-Alloy Steels at 12.4 MPa Pressure

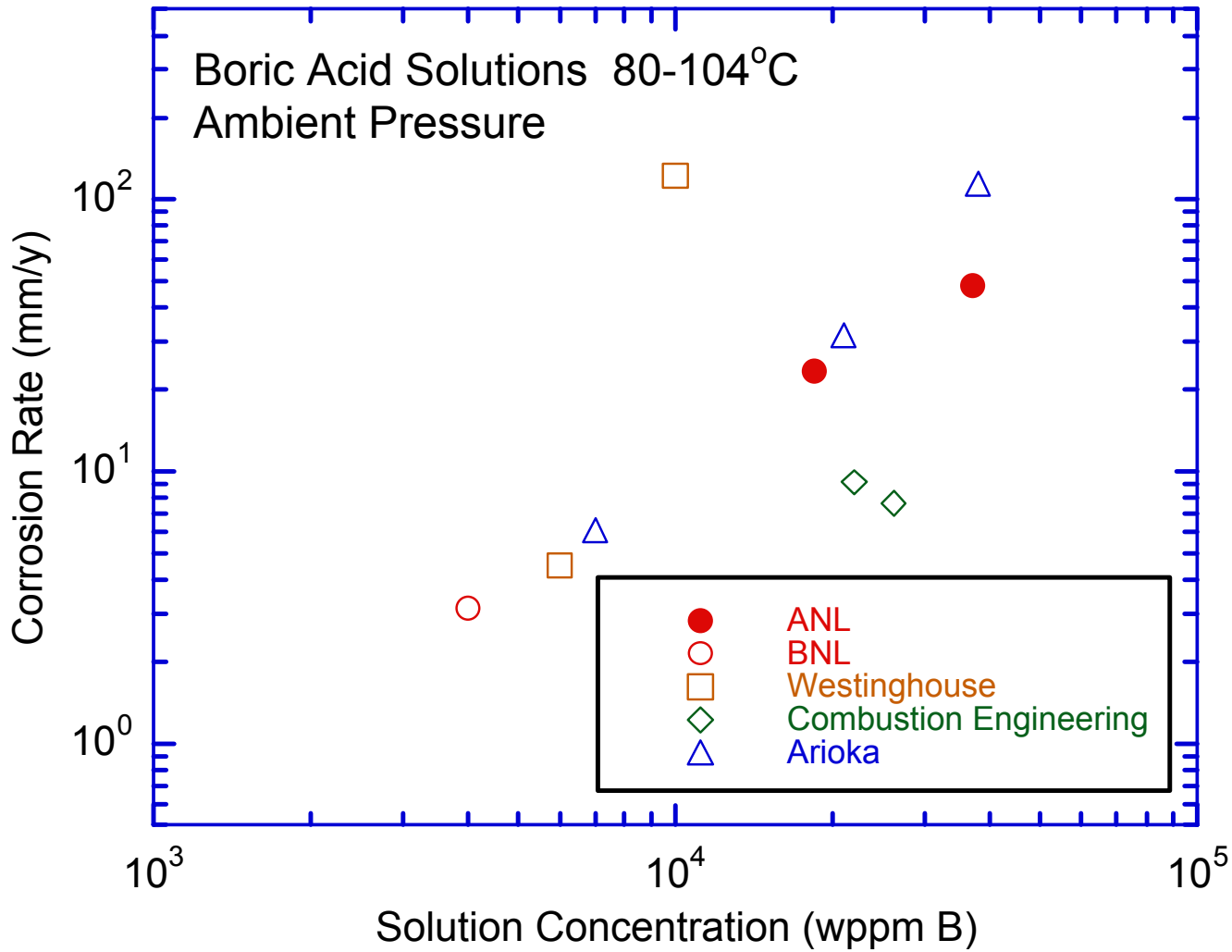


Corrosion Rates

Measured Corrosion Rates for A533-Gr.-B Steel in Various Boric Acid Solutions



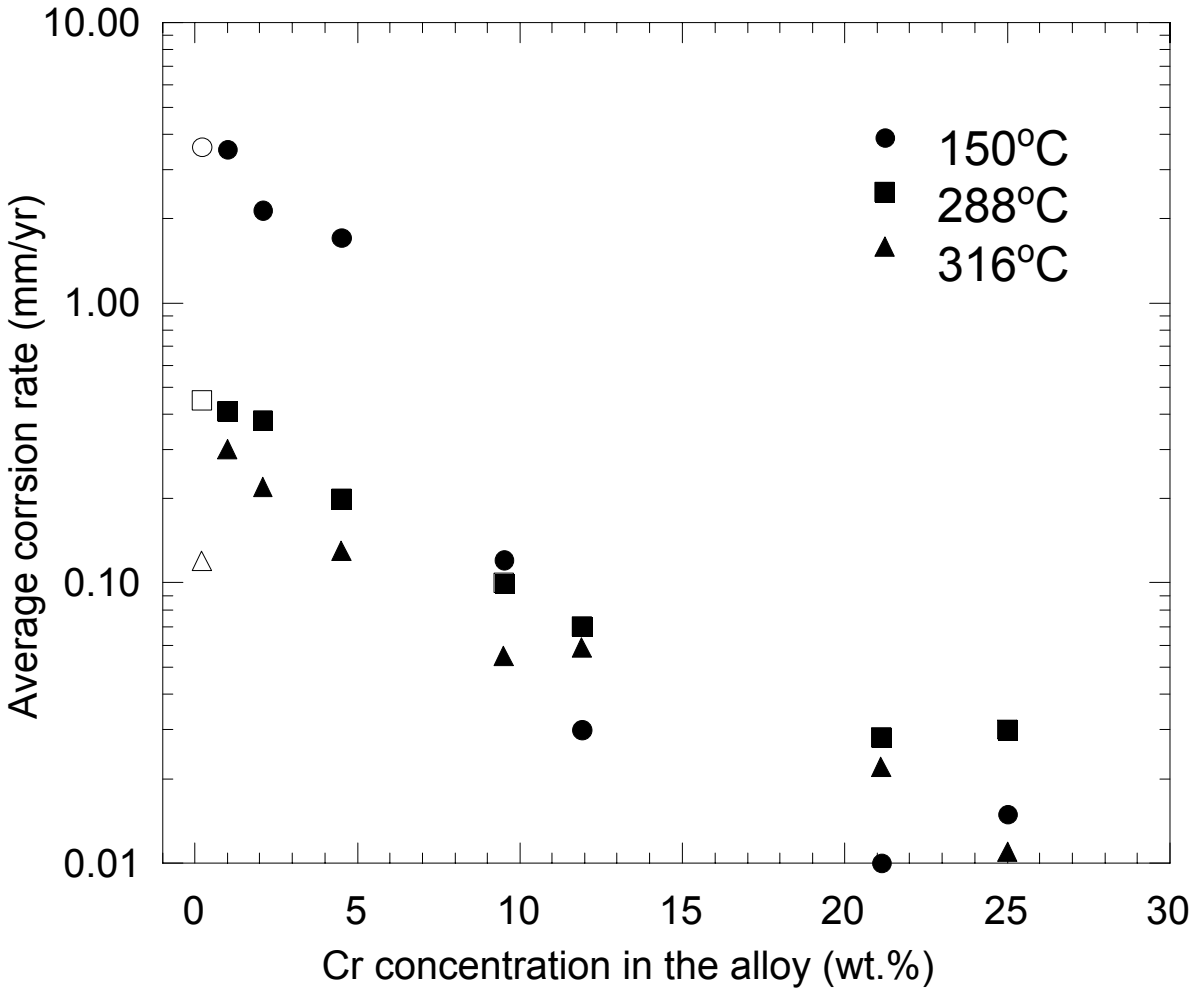
Measured Corrosion Rates for Low-Alloy Steels at 80-104°C



Cr effect: Chemical compositions of the alloys exposed in room-temperature-saturated boric acid solution

Alloy	C	Cr	Mo	Ni	Si	Mn	Nb	V
H-1	0.096	1.0	0.47	0.08	0.09	0.001	0.002	-
H-2	0.096	2.1	0.48	0.06	0.09	0.001	0.002	-
H-3	0.094	4.5	0.46	0.06	0.13	0.005	0.005	0.002
H-6	0.098	9.5	0.50	0.07	0.01	0.002	0.005	0.001
H-9	0.094	11.9	0.49	0.05	0.01	0.001	0.010	-
308SS	0.029	21.1	0.39	9.37	0.56	1.27	-	-

Effect of Cr on average corrosion rate in rt-saturated boric acid solution (9090 wtppm B) at 150, 288, and 316°C and 12.4 MPa under H_2 cover gas



Note: Data indicated by open symbols correspond to A533 steel

Effect of Cr Concentration

- **The effect of increasing the Cr content of the alloy is to lower the corrosion rate at all temperatures of the study**
- **At 150°C, there is a dramatic drop in corrosion rate when the Cr content of the alloy increases to 9 wt.%**
- **The effect of increase in temperature is to decrease the corrosion rate for the same boric acid concentration in the solution and for the same Cr content in the alloy**
- **For a typical 308SS weldment with a nominal Cr content of 21 wt.%, the corrosion rate in room-temperature-saturated boric acid solution is in the range of 0.01-0.03 mm/y. The rate increases to 0.05-0.11 mm/y as the Cr content drops to 9 wt.%**

Summary

- We have developed experimental data on ECP and corrosion/wastage rates for materials used in the RPV head and nozzles of a typical PWR in boric acid solutions of varying concentrations at temperatures of 95-316°C (203-600°F)
- For A533 Gr.-B steel, an average corrosion rate of ≈40 mm/y was measured in aerated saturated solution of boric acid at 97.5°C and ambient pressure; The corrosion rate in aerated half-saturated solution was a factor of ≈2 lower than in saturated solution
- The rates in deaerated solution were ≈40% lower than in aerated solution
- Very high corrosion rates were observed for A533 Gr.-B steel at 140-170°C in super-saturated H-B-O solutions of boric acid with addition of water; short term rates up to 150 mm/y were measured at 150°C

Summary (continued)

- **Corrosion tests in high-temperature high-pressure water containing 9090 ppm B, ≈2 ppm Li, <10 ppb DO, and ≈2 ppm dissolved hydrogen showed rates of ≈5 mm/y at 100-150°C and decreased to <0.1 mm/y at 316°C**
- **The effect of increasing the Cr content of the alloy is to lower the corrosion rate at all temperatures of the study; At 150°C, there is a dramatic drop in corrosion rate when the Cr content of the alloy increases to 9 wt.%**
- **For a typical 308SS weldment (21 wt.%Cr), the corrosion rate in RT-saturated boric acid solution is in the range of 0.01-0.03 mm/y. The rate increases to 0.05-0.11 mm/y as the Cr content drops to 9 wt.%**
- **We have compared the results from this study with data available in literature; current results obtained at 97.5°C are in agreement with data generated in the past at 80-104°C**